Uranium and associated elements detection in carbonaceous shale and dolostone, Southwestern Sinai, Egypt

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ABSTRACT. The uranium occurs in the Lower Carbonaceous shale and dolostone of the Um Bogma Formation, Southwestern Sinai are characterized by visible uranium minerals that observed by the naked eye in the field and associated concentric zonation of Cu, Co, Ni, Pb and Zn elements. The mineralogical studies using X-Ray diffraction and scanning electron microscope attached with EDAX unit identified the presence of the main uranium minerals as triuranium octoxide and uranophane, with associated minerals as Cu-minerals, hematite, Mn-minerals and pyrite. A detailed field and mineralogical study support the hypothesis that the metal source of these mineralization precipitated from hydrothermal fluids related to the magmatic intrusion of basaltic sheets and sills covering the area. The hydrothermal fluids have dominantly concentrated as fissure filling and have been redistributed by meteoric waters postdating the basaltic intrusion stage. The deposits of U, Cu, Co, Ni, Pb and Zn traces as veins and fissure filling are approximately 10 to 20 times higher than in redistributed anomalous other areas. The metals U, Cu, Co, Ni, Pb and Zn occurrences have comparable concentrations for both types of anomalies, which suggests that the fluid sources are compositionally similar and could have derived from the deep-seated magmatic-hydrothermal environment.

1. Introduction

Carbonaceous shale and dolostone of the Um Bogma Formation are sedimentary rocks formed by consolidation under conditions and the presence of organic matter, representing residues of algae and bacteria that lived in the sea.

Mineralization in carbonaceous shale and dolostone of Um Bogma has resulted in one of the largest ore deposits in the area, especially uranium, copper, iron and Mn occurrences. The currently mineralization shale and dolostone contain uranium veins and layers with a strike length of several meters related to the Um Bogma Formation. Above and below this Formation-rich uranium body are Abu Thora and Adadia formations respectively.

The studied area ‘Figure 1’, which is known as Um Bogma environs, is now exhausted mined for ferromanganese minerals, and selected to collect the representative samples from the main uraniferous layer of carbonaceous shale and dolostone of Carboniferous age. This study deals with the geology, mineralogy and textures of the uranium assemblage, and their relationships have allowed us to put some limits on the behavior of the late-stage uranium and associated elements mineralization.

2. Geologic setting

Carbonaceous shale and dolostone of the Carboniferous age occur in Paleozoic units in the South Sinai blocks of the Um Bogma Formation, although their characteristics are greatly different from block to block. The Um Bogma Formation contains an abundance of mineralization and organic carbon-rich (up to 10 wt.% carbon) [1]. Some of these carbonaceous shales are extremely metal-rich and can be traced

along strike for tens of meters and remark that this type of black shale deposit may have significant suggestions for exploration in like environments, e.g., Nick Property, Yukon, Canada [2].

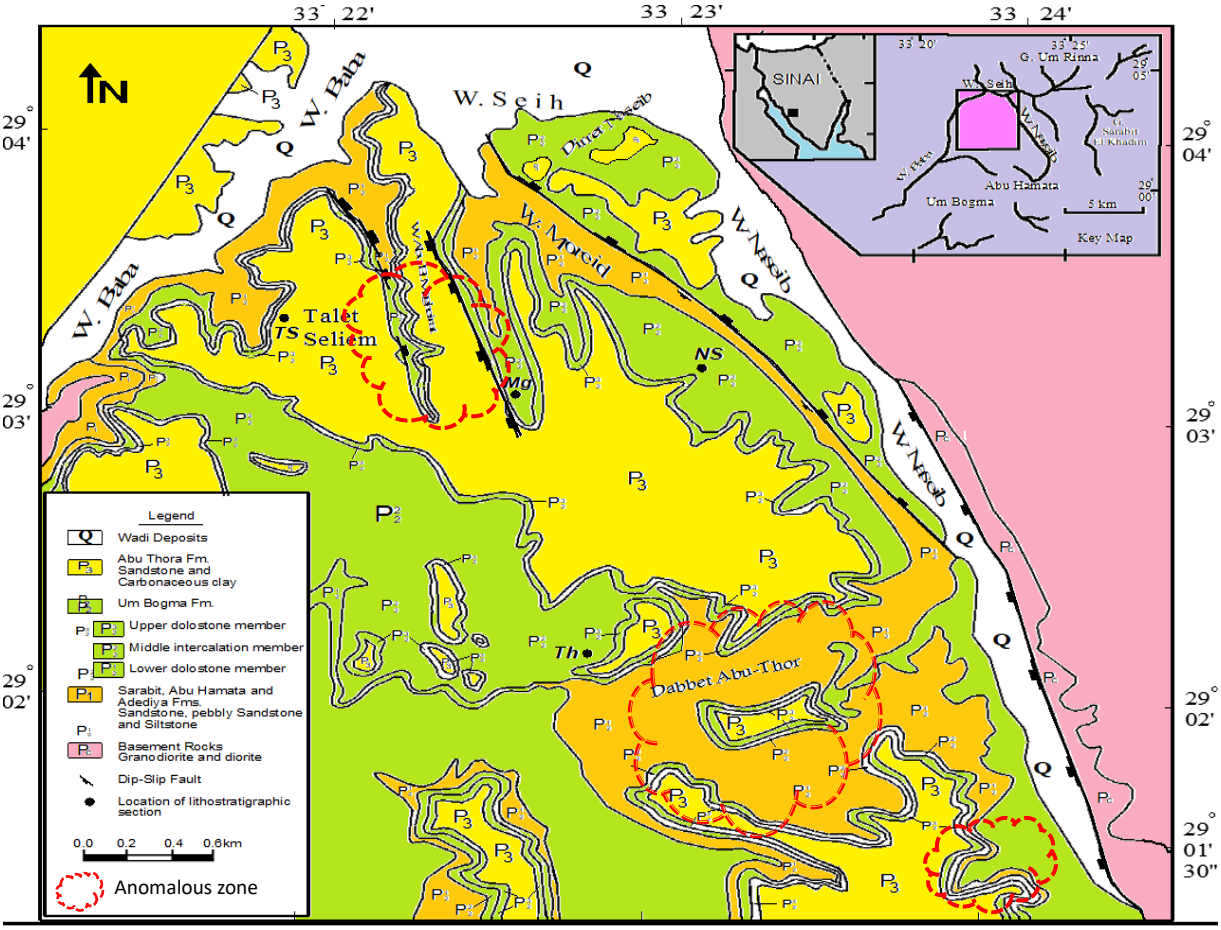

Figure 1. Geologic map of the studied area of the Um Bogma Formation environs, southwestern Sinai

The source of the associated element of uranium-rich Um Bogma Formation has attracted attention for more than 50 years since the first description by NMA exploration group. [3] and [4] referred to the occurrence of the uranium minerals torbernite, zeunerite, zippeite and uranophane associated with Cu and Mn mineralization. [1] recorded umohoite, moluranite, sedovite, bassetite, brannerite, torbernite, jarosite, willemite, kaolinite, hematite, goethite, pyrite, galena and barite in the area.

The carbonaceous shale and dolostone of the Um Bogma Formation are located unconformably between the underlying sandstones and shales of Adedia Formation and overlying the non-fossiliferous sandstones of the Abu Thora Formation. Ferromanganese minerals associated with the carbonaceous shale and dolostone are widely mined in the area and rich in a high content of organic matter, which is one of the basic components of the uraniferous area ‘Figures 2A&B’, and increased within and around the small-scale fault planes.

The most important uraniferous horizons in the area are the carbonaceous shale and dolostone, which agree with [5], [6], [7] & [8]. The rocks are characterized by the presence of accumulation of cubic and framboidal pyrite with yellow native sulphur, which detected by the naked eye in representative samples in the field. According to [9], framboidal pyrite is very common in reducing sediments, such as modern dark muds or in the ancient dark shales and limestones.

According to the field observation, the carbonaceous shale and dolostone are dominant in the middle and lower members of the Um Bogma Formation and generally exhibit two different bedding

occurrences. The upper dolomite beds are intercalated with carboniferous shale, while the lower dolomite is massive and laterally changes in thickness and is characterized by fracture filling by gypsum veins ‘Figure 2C’ and calcite vugs filling ‘Figure 2D’. The calcite veins and vugs filling zones within the black dolostone have a rosy-bright color and are highly radioactive. [7] reported that the calcite veins seem to be much later than the dolomitization process and can be divided into two steps: (1) dissolution of dolomite in fissure; and (2) the precipitation of calcite to form the coarse rhombic crystals with the solution with high uranium, manganese and copper content.

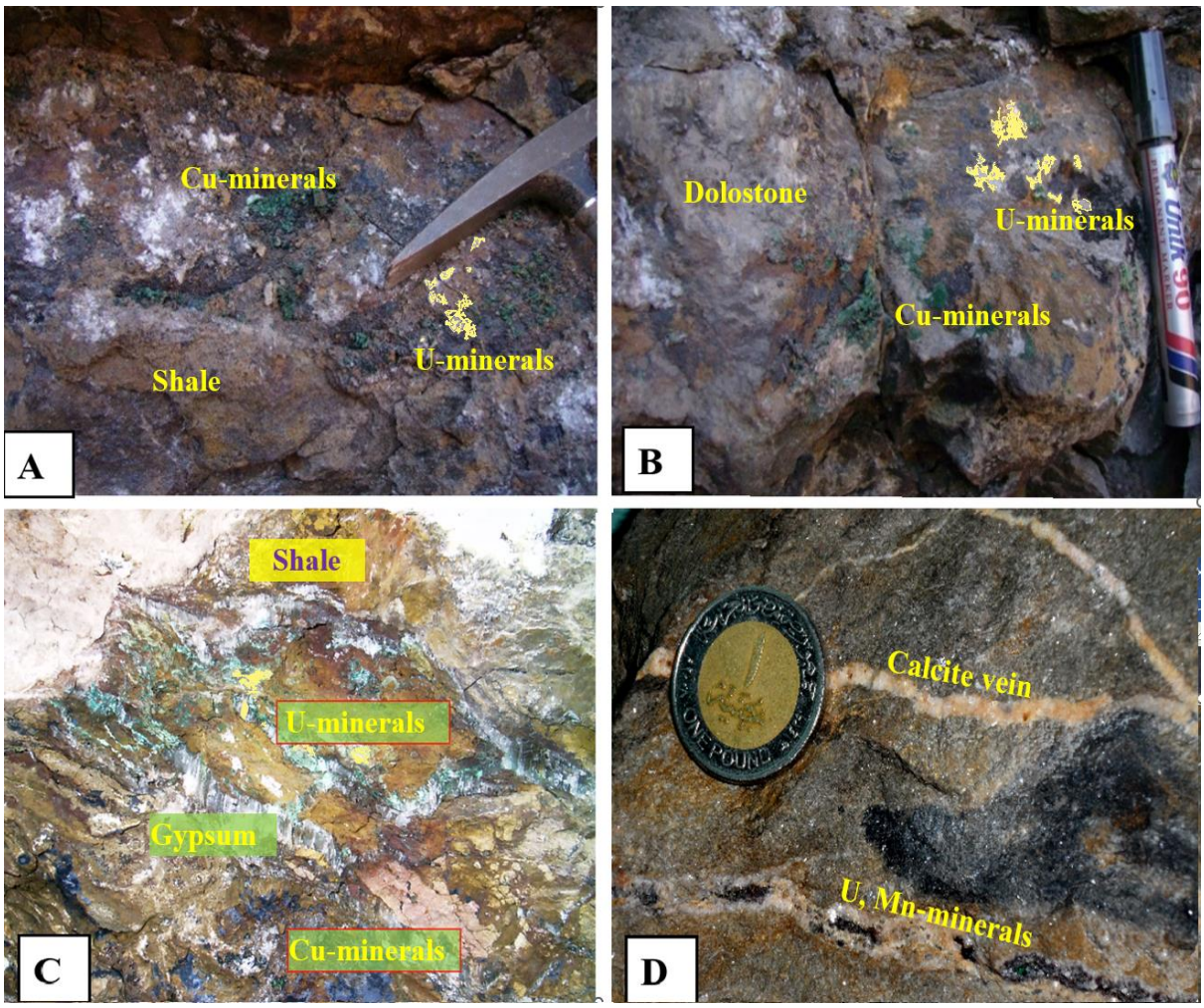

Figure 2. Photographs of representative samples show A- Vugs filled by uranium and Cu surrounded by organic matter. B- Fracture and vugs filled by organic matter. C- Gypsum crystals veins contain Cu, and uranium minerals. D- Calcite veins rich in uranium minerals in dolomite.

3. Exploration and identification Methods

X-ray fluorescence (XRF) in uranium and associated elements exploration geochemistry is one of the most common rapid methods for qualitative methods in mineral exploration by determining the elemental composition of ore materials. This technique is an extremely suitable indication analysis for rocks or powders and can be used to measure many elements at the same time. Mineral examination and preliminary identification were done on picked separated grains after heavy liquid separation with the scanning electron microscope using an energy-dispersive X-ray spectrometer (EDS) for elemental composition. The samples were examined optically and by (BSE) back-scattered electron imaging to define every point for analysis.

3.1. X-Ray Fluorescence Analysis

In the field exploration, portable X-ray fluorescence analysers (Table 1) were used for on-site data acquisition. The typical ore metal analyses of the mineralization zone within the Um Bogma area are Pb, Zn, Ni, Co, U and Cu, although the surrounding hosting rocks vary in content.

Table 1: Summarized chemical data of uranium and associated elements in the Um Bogma representative samples from mineralized zones by portable X-ray fluorescence analysers.

Samp. No.	Pb (ppm)	Zn (ppm)	Ni (ppm)	Co (ppm)	U (ppm)	Cu (ppm)
T1	95	2489	218	529	519	1078
T2	81	3309	223	505	373	1068
T3	76	372	131	348	488	9709
T4	78	2440	157	335	392	9606
G1	36	2563	235	426	951	9556
G2	113	723	241	424	449	8997
T5	3669	1088	1393	1832	131	8694
T6	128	7045	2168	4940	241	8519
T7	79	2634	3645	818	208	7973
T8	40	5121	573	751	146	6582
T9	42	1133	669	872	95	5783
G3	54	700	136	214	655	5069
T10	4549	6232	1249	3205	124	4527
T11	1771	3676	760	1762	565	4425
G4	51	56	60	192	389	4400
T12	3179	6789	1028	2924	178	4252
T13	111	1207	1777	710	563	4241
T14	407	5793	681	103	104	4133
T15	2753	3366	826	2050	493	4100
H1	89	1504	183	149	479	3986
T16	6557	5371	1434	3927	115	3865
T17	1982	5046	1000	2646	127	3842
T18	4148	6093	1194	3499	77	3675
T19	656	4861	623	345	153	3565
T20	3182	5962	874	2131	136	3507
G5	30	59	60	172	269	3378
T25	174	1636	1802	217	214	3374
G4	56	750	378	699	87	3304
G5	43	988	291	206	380	3242
G6	146	445	50	34	859	3121
G7	35	244	51	84	165	2818
T21	82	9809	1313	144	68	2573
G8	85	179	43	23	605	2498
T22	61	1313	295	305	35	2392
T23	2068	1410	580	1299	232	2371
H2	125	9491	1579	2064	103	2275
H3	48	805	208	478	28	2072
T24	2417	3453	242	425	105	2027
T25	5761	6281	852	1890	57	1996
Av	2264	4304	899	1819	269	4040
Min	85	56	43	23	28	1068
Max	6557	9809	3645	4940	951	9709

The zinc contents range from 56 to 9809 ppm of the mineralization zone, with an average of 4304 ppm through the mineralized zones, and the copper contents are occasionally enriched and range from 1068 to 9709 ppm, with an average of 4040 ppm through the mineralized zones. Nickel is occasionally enriched up to some hundreds of ppm. The cobalt contents range from 23 to 4940 ppm in the mineralization zone, with an average of 1819 ppm through the mineralized zones. Uranium content ranges from 28 to 951 ppm; the average is 269 ppm in the uraniferous mineralization, in which the lead content reaches 6557 ppm. The uranium and lead content tends to be very low in the country rocks (less than 20 ppm). So, it has been proposed that the source of the higher lead contents related to the mineralized uraniferous zone is radiogenic. Historically deposits of uranium, in order to be considered economic, should contain at least 700ppm of U_3O_8, but grades lower than 700ppm can be profitably treated if they contain a valuable by-product of associated elements [10] and can be economically processed for uranium recovery, even though their feed grades are only in the vicinity of 250 ppm U_3O_8 [11]. Thus, by processing ore at a rate of 35000 t/d, the Rossing operation in Namibia is able to treat ore with a head grade of 350ppm of uranium profitably [12].

It is worth mentioning that the studied associated elements (with higher grade values) are present in some zones of low-grade uranium deposits, which may upgrade them to economic values. Accordingly, the uranium zones ore bodies in the area will be of higher potential economic value attributed to the associated valuable elements, according to preliminary estimation.

4. Mineralogical analysis of the uraniferous sample

The main uranium minerals identified by the XRD data are triuranium octoxide associated with pyrite, hematite, calcite, gypsum and magnetite. Pyrite is the only sulfide mineral identified by the XRD analysis, and the other sulfide minerals of Cu, Co, Ni, and Zn may be present in the shale matrix, but in very minute quantities, which are not detectable by the powder X-ray diffraction method.

4. Triuranium octoxide (U_3O_8)

Uranium minerals are the main mineral in the zoned mineralized area ‘Figure 2B&D’. A picked crystals of these mineral grains were carried out for X-ray diffraction analysis, which illustrates the matches data of triuranium octoxide card No 2-0267 ‘Figure 3’. The triuranium octoxide is an abundant uranium mineral present in fractures associated with magnetite and calcite veins in the representative samples. According to [13], Pb and Ca have both substituted for U in the UO_2 cubic lattice in varying amounts across the uraninite grains and veins.

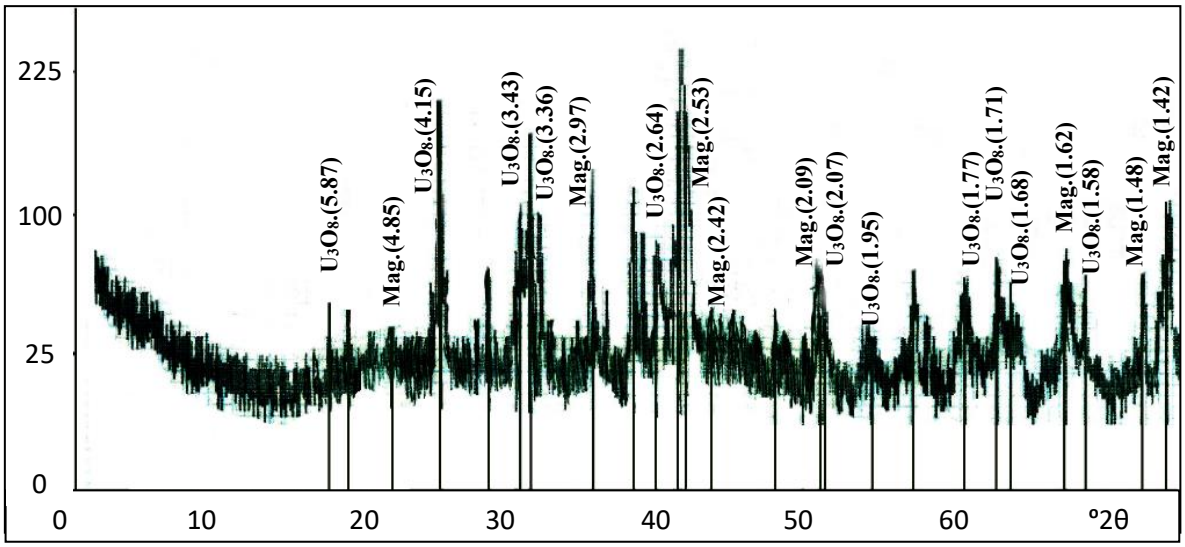

Figure 3. X-ray powder pattern showed that the major constituents of the concentrate are triuranium octoxide (U_3O_8), JCPDS card (2-0267) associated with magnetite JCPDS card (19-629).

The uranium grains were subjected to the scanning electron microscope attached with an EDAX unit ‘Figure 4’, which shows that the U, S and Fe are the main components. The presence of Fe and S is attributed to the abundance of pyrite and iron oxide, which are found associated with uranium.

4.2. Pyrite

The pyrite grains are subhedral and framboidal, scattered throughout the matrix of the calcite veins ‘Figure 2D’. The pyrite and calcite crystal associations in veins may be from hydrothermal fluids that pass through the fissures vein precipitating calcite and pyrite, followed by precipitating the organic matter in cavities. Pyrite and black carbonaceous shale represent a reducing facies (redox-front) at which the migrated hexavalent uranium from the surrounding rocks can reduce to the tetravalent state, resulting in the redeposition of the primary uranium minerals ‘Figure 4’.

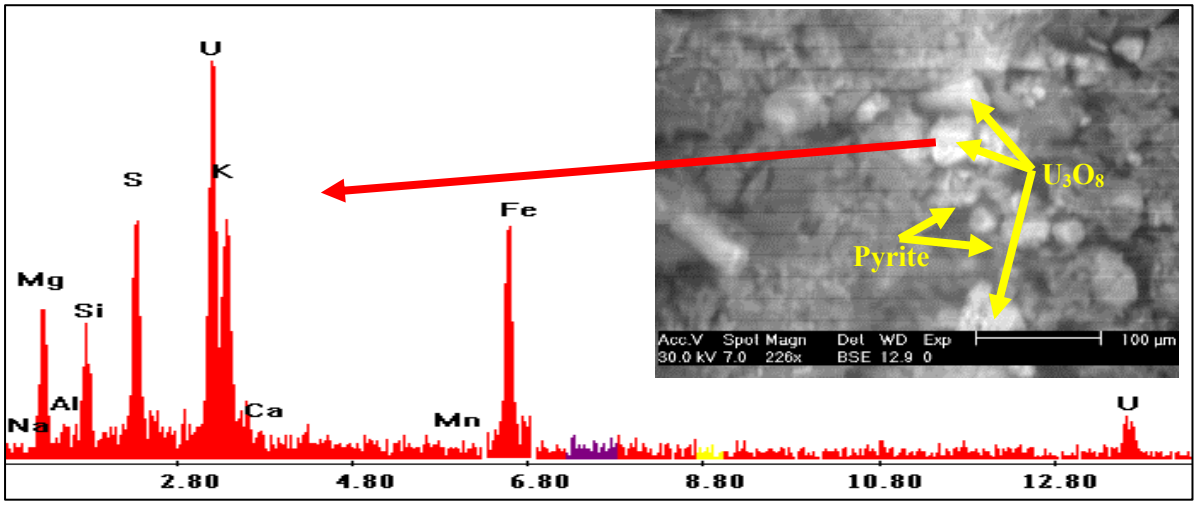

Figure 4. BSE image showing the photo image and the chart of the analysed grains of triuranium octoxide and pyrite minerals.

The ESEM analysis ‘Figure 5’ was used to characterize the chemical composition of triuranium octoxide. The EDAX results indicate that the crystals contain a variable content of uranium, which fluctuated between 54.0% and 66.6% in different samples.

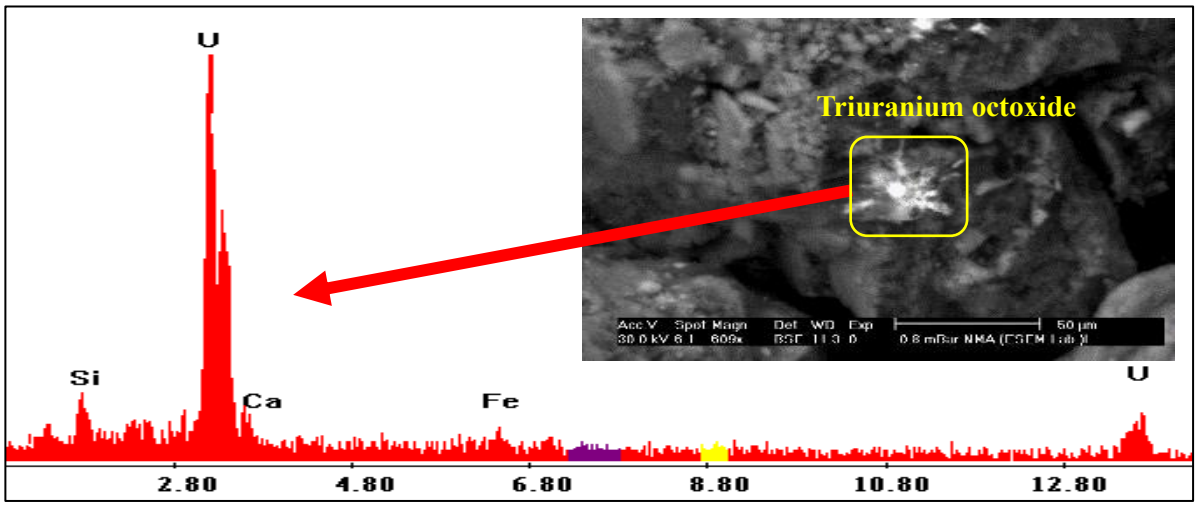

Figure 5. BSE image and the (SEM-EDX) analysis pattern of triuranium octoxide (very bright appearance).

4.3. Uranophane **($Ca(UO_2)_2SiO_3$)**

Uranophane occurs as anhedral to subhedral fine grains of a straw-yellow color with fibrous radiating crystals. The X-ray diffractogram of the selected picked crystals 'Figure 6' illustrates the matches pattern of uranophane (card No. 4-556). However, uranophane appears as small patches associated with other minerals as gypsum ($CaSO_4 \cdot 2H_2O$), as shown in BSE Scanning Electron Microscopy, which can be interpreted as the chemical substitution stage between gypsum and primary uranium minerals as triuranium octoxide (U_3O_8). Uranophane is much scattered within the dolomite vugs and cracks exist in tiny sizes and are also found in separate well well-developed, radiated crystals. It also forms collections of needle-shaped crystals as image in figure 7. Uranophane rarely occurs in some parts as lemon-yellow radial masses in the cavities along the rock as an intergrowth of minute fibers in a fan form. The EDX data indicate that uranophane crystals contain up to 36.2% U and 15.2% Si and 17.8% Ca, with variable concentrations of Al, Fe and K elements 'Figure 7'.

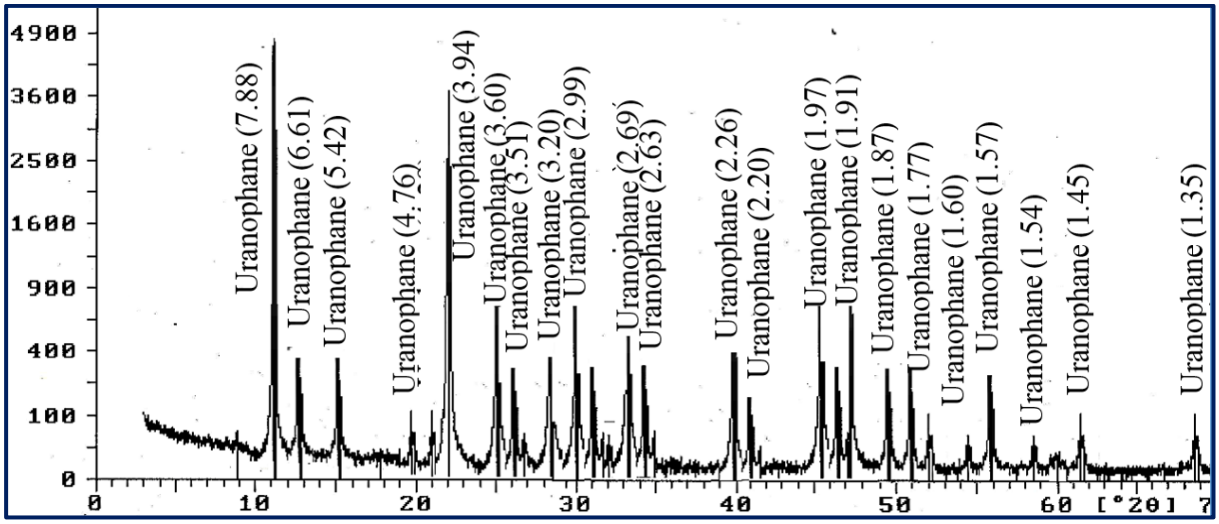

Figure 6. X-ray powder pattern diffractogram of uranophane mineral, which showed that the identification was confirmed by matching the ASTM card No. (8-442).

5. Interpretations of the uraniferous ore surface

Gypsum ($CaSO_4 \cdot 2H_2O$) is the most common calcium sulfate-bearing mineral that appears as veinlets in fissures and the surface of radioactive zones in the area 'Figure 2C', as gypsum fissure filling crystals veins contain Cu, and uranium minerals, and from the peripheries of veins cutting across the shale and dolomite rock. The crystals of gypsum are commonly elongated, white to pale green, have a vitreous luster, and appear transparent to translucent. The main feature in the uraniferous ore surface is the earthy white color sediments (Hydrated calcium sulfate), which cover the exposed parts of the uraniferous zone 'Figure 2C'. These white sediments are of evaporate, which results from pyrite oxidation and bacterial reactions. Bacterial oxidation of pyrite yields sulfuric acid (H_2SO_4) and iron as ferrous iron (Fe^{2+}) in the form of ferrous sulfate ($FeSO_4$) [14]. Bacterial oxidation of pyrite is an acid-generating reaction. The formation of gypsum ($CaSO_4 \cdot 2H_2O$) due to the reaction of H_2SO_4 with calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Gypsum ($CaSO_4 \cdot 2H_2O$) is precipitated as a solid reaction product with water-soluble magnesium sulfate (MgSO4) and carbon dioxide as a gaseous. The main components of this precipitate are gypsum ($CaSO_4.2H_2O$) compounds, 'Figure 8'. These hydrated calcium sulfate (gypsum) components, which were formed on the surface of the ore material are cover the surface of different uranium minerals of the uraniferous zones.

Based on the field investigation and mineralogical study on control factors of uranium mineralized forms, it is indicated that all the occurrences of main uranium mineralization types are controlled by strata, structure and fissure filling as well as closely related to oxidation zone in the area and the structures is the main factor for controlling uranium distribution.

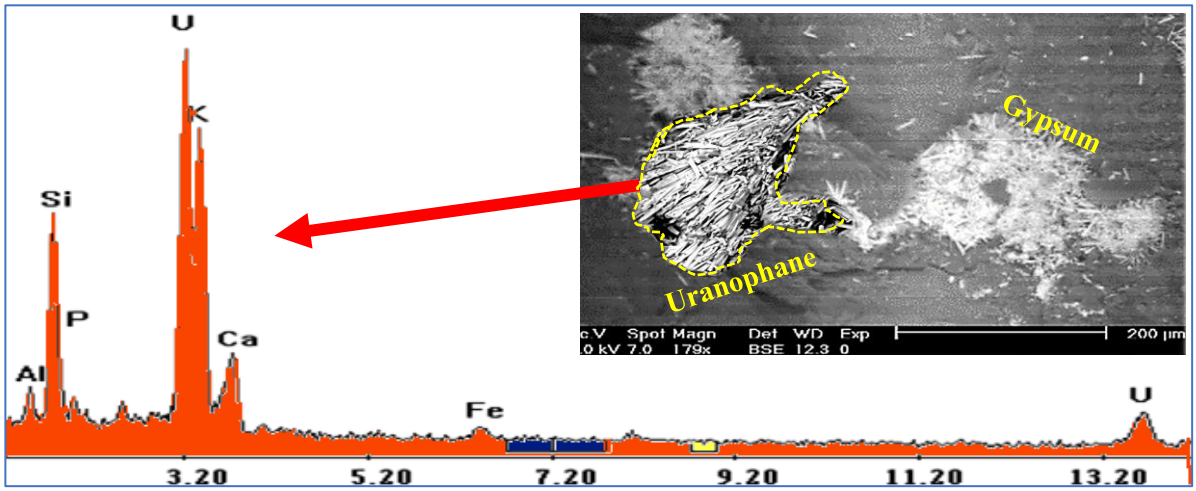

Figure 7. SEM with backscatter image of the analysed grains of uranophane mineral.

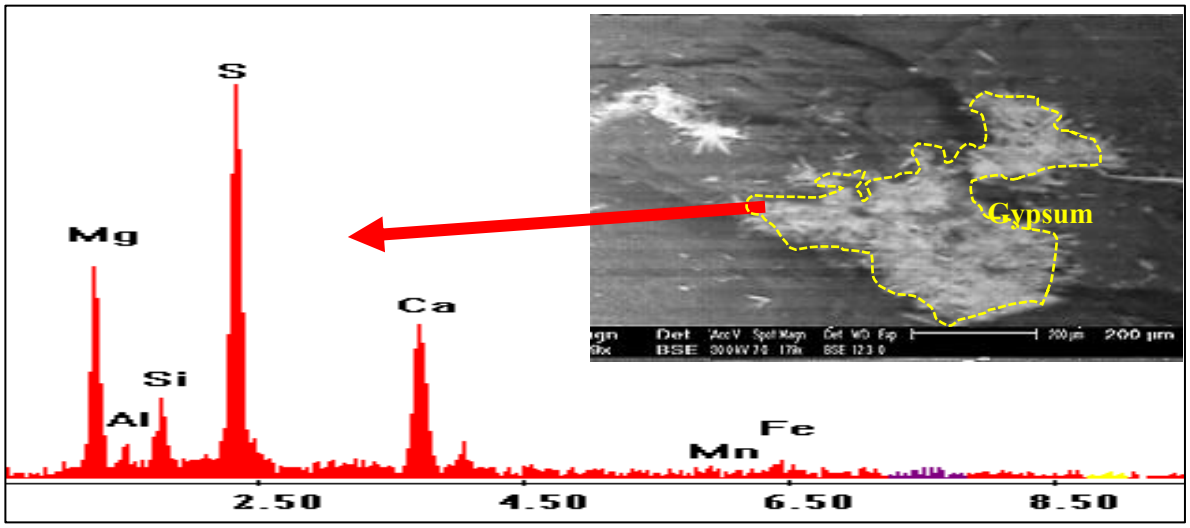

Figure 8. SEM with backscatter image of gypsum from the surface of uraniferous zones

From XRF exploration geochemically for uranium (Table 1), the uranium measurements of the major anomalous zones are higher grade ones (with U grade more than 100ppm) distributed widely in the area, with large resources. It would make a big contribution to development if these lower-grade uranium resources could be fully used. The associated elements as Cu, Co, Ni, Pb and Zn, are very precious, and in the case of recovering these associated elements, which also provides a possibility to lower the cutoff grade of the uranium types ores.

6. Conclusion

The most noticeable uranium zones in the Um Bogma Formation are related to carbonaceous shale and dolostone of the sandstone-type deposit. The thickness of the uraniferous zones of the Um Bogma Formation, which contain the ore bodies, varies from 1 to 8 m in the anomalous areas, and it reaches 100 Km^2 in the distributions [15] and [16]. The uraniferous zones are sulfide-poor and often associated with Co, Ni, Cu, Zn and Pb. The main associated minerals are pyrite, hematite and gypsum, with minor magnetite and triuranium octoxide. Zn, Ni, Cu and Co are the most promising metals for exploitation in deep fractures in the epigenetic ore-forming processes that have been very important in the uraniferous zones. The main uranium minerals, triuranium octoxide and uranophane, occur in the matrix and along

the veins boundaries, associated with some sulphide minerals, mainly pyrite, also occur within the mineralization zones. The enrichment of uranium in uraniferous zones is 10 to 100 times higher as compared with the background values of the hosted country rocks. Co, Cu and Ni contents are roughly the same as those of uranium, with a positive correlation between uranium and associated elements. According to this study, which describes the uranium occurrences and behavior of uranium and associated elements with organic matter of carbonaceous shale and dolostone in uraniferous zones, the assemblage of the principal uranium and associated minerals represented in the matrix and somewhat fractured, suggesting that mineralization of the area were related to hydrothermal activity. Biological oxidation of sulfide minerals as pyrite, generates sulfuric acid and ferric sulfate during the groundwater movement process. This process partial leaching of uranium and associated minerals, which leads to the redistribution of uranium in other places. The results of this study could be very useful for helping in the exploration and mining process of uranium and associated metals as by-products from carbonaceous shale and dolostone of the Um Bogma Formation.

7. References

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