

Primary uranium mineralization in paleochannels of the Um Bogma Formation at Allouga, Southwestern Sinai, Egypt.

Amer Hussien Bishr

Nuclear Materials Authority, P.O.Box 530, Maadi, Cairo, Egypt.

معادن اليورانيوم الاولية في القنوات القديمة لمتكون ام بجما في منطقة
العلوجة، جنوب غرب سيناء. مصر.

عامر حسين بشر

هيئة المواد النووية - ص ب 530 المعادي - القاهرة - مصر

ملخص

تقع منطقة الدراسة ممثلة في متكون ام بجمة بمنطقة العلوجة داخل الاخدود باتجاه شمال
شمال غرب- جنوب جنوب شرق. وغالب الضخور التي تمثل ام بجمة عبارة عن صخور
الدولوستون (dolostone)، الحجر الجيري (limestone)، المارل (marl)، وصخر الطين
(shale)، الغني بالمواد العضوية والتي تعتبر ذات اهمية في اختزال اليورانيوم السداسي
الى يورانيوم رباعي وترسيبه في صورة معادن يورانيوم اولية. وتتواجد هذه المعادن بكثافة
حول الصدوع الصغيرة داخل المتكون وحول المواد العضوية بالقنوات القديمة. وقد تم
التعرف في هذه الدراسة على معادن اليورانيوم الاولية من اليورانيننت، والبتشبلند والكوفينيت
لاول مره في رسوبيات المنطقة.

Abstract

The Um Bogma Formation in the Allouga area is within a major graben trending NNW-SSE. The formation is composed mainly of sandy-dolostone, limonitic marl, siltstone and carbonaceous shale with a high content of organic matter. The black carbonaceous shale represents the redox-front (reduced facies) at which hexavalent uranium can reduce to the tetravalent state, resulting in the redeposition of uranium minerals. The presence of uranium minerals are increased with an increasing amount of carbonaceous matter in the paleochannels of the Allouga area. Small-scale fault planes also show an increase in the uranium content. The present study reveals the presence of the primary uranium minerals; uraninite, pitchblende and coffinite, which are recorded for the first time in the area.

Introduction

Southwestern Sinai has attracted the attention of many studies, when it was identified as one of the principal source of uranium minerals in Egypt. [1] and [2] reported the occurrence of the uranium minerals torbernite, zeunerite, zippeite and uranophane associated with Cu minerals and Mn oxides. [3] Referred to the presence of umohoite, moluranite, sedovite, bassetite, brannerite, torbernite, jarosite, willemite, kaolinite, hematite, goethite, pyrite, galena and barite in the area.

The present study is mainly concerned with the identification of primary uranium (U^{4+}) minerals as a new addition for the previously mentioned secondary uranium (U^{6+}) minerals in the Carboniferous sedimentary rocks in Sinai. The identification of primary uranium minerals in the area has been made using general physical properties, X-ray powder diffraction and SEM-EDS analyses.

Geologic setting

The sediments of the Um Bogma Formation are exposed 40 Km east of Abu Zinema City in Sinai (Fig. 1) and the formation lies unconformably over the Adedia Formation (sandstones and shales), and is itself unconformably underlain the non-fossiliferous bleached sandstones of the Abu Thora Formation.

The Um Bogma Formation consists of carbonaceous black shale, sandy-dolostone, limonitic marl, and siltstone and is exposed in the Allouga area (Fig. 1), with several mineralized layers. Ferromanganese minerals within the basal part of Um Bogma Formation have been widely mined for many years. The carbonaceous matter is one of the basic components of the shale-bearing sandy-dolostone in the Allouga area. The carbonaceous shale is distributed as patches through the sandy-dolostones of the middle member with different degrees of oxidation. The variegated shale changes from purple red to grayish black and black in color. The grayish black shale is characterized by the presence of framboidal pyrite and yellow native sulphur that can be observed by the naked eye in the field, with framboidal pyrite increasing with increasing depth. According to [4], framboidal pyrite is very common in reducing sediments, such as modern dark muds, or in ancient dark shales and limestones.

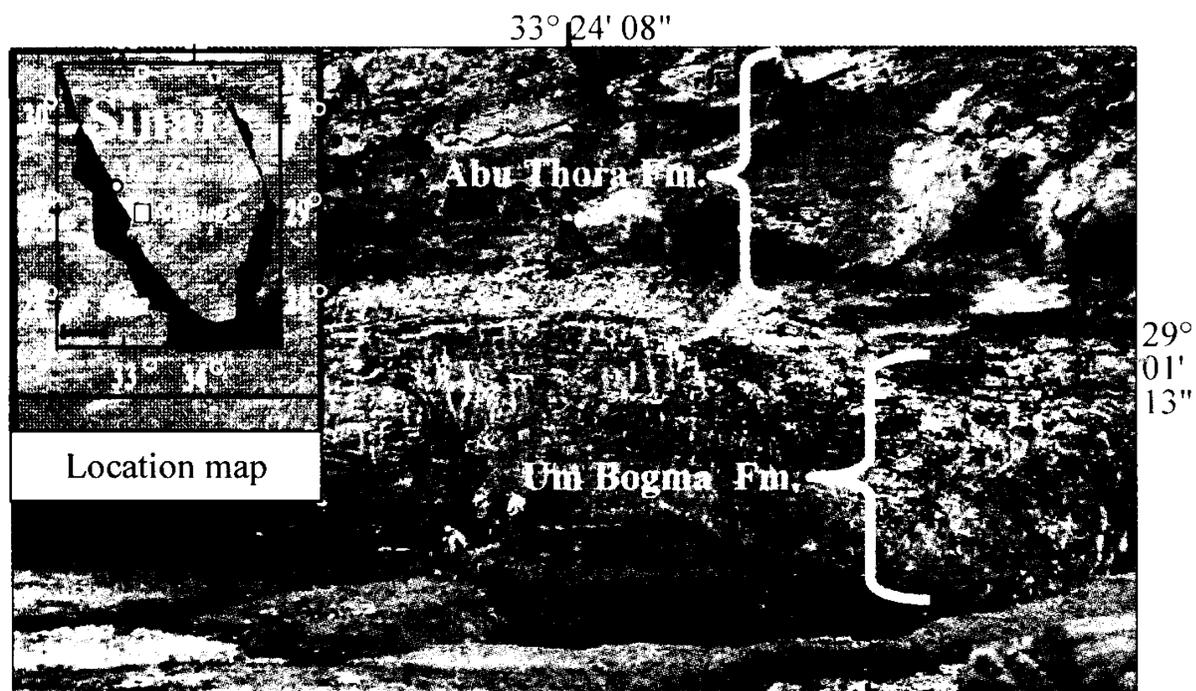


Fig. 1. Location map and the Um Bogma Formation in Gabal Allouga.

A spatial relationship is evident between areas of high uranium in basement rocks and uranium mineralization within the overlying sediments, for example, paleochannel uranium may be sourced from uraniumiferous basement rocks. The Allouga area is included within a major graben surrounded by high mountains of granite which may also constitute the basement rocks to the graben. In the Allouga area, uranium contents of granite rocks at Wadi Um Hamd to the south of the Um Bogma area are high [5].

Radioactivity

The high radioactivity of the Um Bogma Formation is mainly due to the presence of uranium mineralizations, which can be classified into primary and secondary minerals. The primary form occurs as heterogeneous submicroscopic crystals scattered in the carbonaceous shale-bearing sandy-dolostone. The secondary uranium minerals are present as adsorbed uranium on other secondary phases produced during alteration. They are also present as fracture-filling materials or along grain boundaries, adsorbed from uranium-bearing solutions, which migrated along deformation features, including faults. The face of the Allouga quarry was radiometrically surveyed (Fig. 2) and the resulting radiometric contour map for eU shows the presence of intensive

anomalous zones reaching up to 4000 ppm eU. The distribution of these highly anomalous zones is mainly associated with carbonaceous shale-bearing sandy-dolostone and governed by small-scale faults.

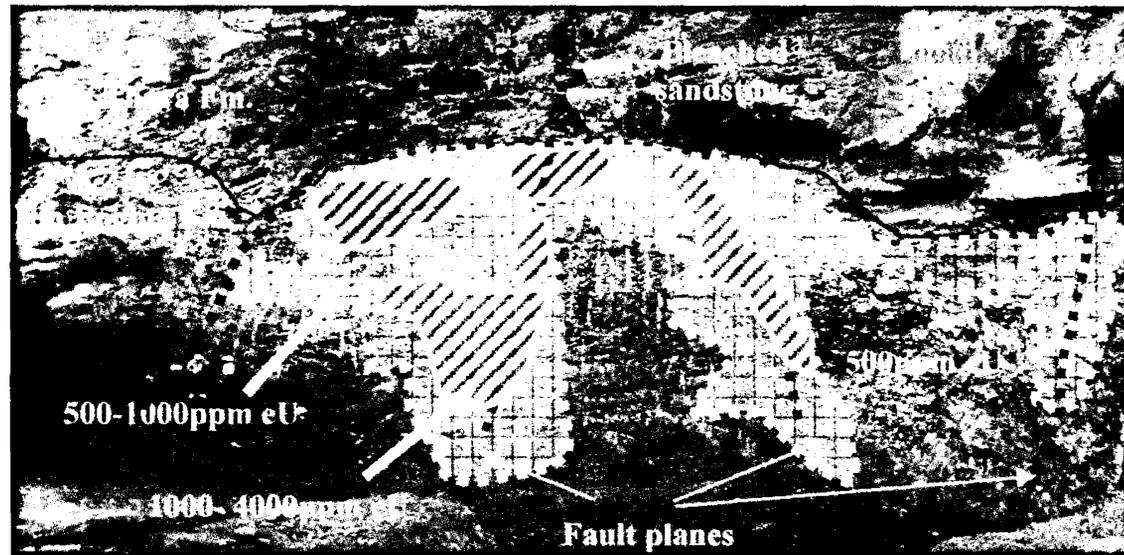


Fig. 2. Delineation of the ore body at the Allouga Quarry.

Categorization of Allouga uranium deposit.

The categorization of the Allouga uranium ore deposit is based mainly on its geological setting, shape, mineralogical characteristics, uranium content and relationship with the depositional environment. According to these parameters, the uranium deposit at the Allouga quarry can be categorized as a paleochannel uranium deposit.

The term paleochannel-related uranium deposit encompasses three subtypes: sandstone, surficial and lignite [6]. Sandstone uranium deposits are described as an epigenetic concentration of uranium minerals [generally uraninite (UO_2) or coffinite ($USiO_4$)], typically hosted by fine- to coarse-grained sediments deposited in fluvial, alluvial, lacustrine or marginal marine environments. They constitute about 18% of the world's uranium resources (e.g. United States, Niger and Kazakhstan; [7]; [8]). Sandstone uranium deposits can be further subdivided into three types (these may be gradational into each other): tabular, roll-front and tectonic-lithologic [9]. Tabular and roll-front mineralized bodies generally appear along the contact of sandy rocks and intercalated clay horizons and at paleochannels margins, while tectonic-lithologic deposits may occur in sandstones adjacent to a permeable fault zone. Precipitation of uranium minerals in most tabular deposits is thought to begin shortly after sedimentation and burial processes [6]. The uranium

in the Allouga area may be carried by surface water from host granite rocks during which mineralized solutions migrate under oxidizing conditions through structural weaknesses and get redeposited within paleochannels zones. These zones are adjacent to permeable small faults through which the mineralizing solutions migrate. Uranium mineralization results from the interaction of uranium-rich oxidizing fluids with reduced lithologies (redox fronts). Sediments in close proximity to the redox boundary typically show yellow to orange coloration resulting from iron oxyhydroxide staining on the oxidized side of the redox boundary, changing progressively towards darker tones within the reduced sediments [6].

Mineralogy

Several samples were collected from the highly anomalous zones in the Allouga Quarry and crushed followed by heavy liquid separation and then hand-picking under the microscope. The primary uranium minerals are very fine-grained, often sub-microscopic. For this reason, the identification of the different minerals has been done on the basis of radioactive and physical properties, followed by X-ray diffraction (XRD) combined with chemical analyses using a Scanning Electron Microscope attached with an EDAX microanalysis unit. The data obtained reveal the presence of the following minerals.

Primary uranium minerals: Uraninite and coffinite occur in micro-scale forms. Both mineral types contain remnants of partly corroded iron grains and copper minerals in close proximity to sulphide minerals. The two important primary ore minerals are uraninite (basically UO_2) and pitchblende (U_3O_8) [10].

Uraninite (UO_2); this is the first time this mineral has been recorded in the Um Bogma Formation in Sinai. The identification of uraninite was confirmed by X-ray powder diffraction of carefully selected fragments from crushed highly radioactive black grains, which were obtained from the heavy mineral fraction. The X-ray diffraction gives a weak pattern (due to being metamict) and matches the Joint Committee on Powder Diffraction Studies (JCPDS) data card 5-550 for UO_2 (Fig. 3A) obtained before heat-treatment, and a combination of UO_2 and U_3O_8 patterns after heating separated from air (out of contact with oxygen). The d-spacing is generally intermediate between JCPDS card (13-225) and (5-550). The X-ray diffraction (Fig. 3A) shows that the major mineral present is uraninite and small associated peaks corresponding to pitchblende are

visible at 4.15 and 2.64 (angles of 24.78 and 42.67 2θ). Other X-ray powder patterns showed a phase of transformation results from exothermic reaction between uraninite, pitchblende and coffinite associated with barite (Fig. 3B). After heating to 800°C for three hours, the X-ray powder pattern showed that the major constituents of the concentrate are pitchblende (triuranium octoxide) U_3O_8 associated with magnetite (Fig. 3C), with small associated peaks corresponding to brannerite visible at 3.27, 2.52, 2.32, and 1.87 Å. Still weaker and less defined peaks, probably relate to trace amounts of a variety of uranium hydroxides. Uraninite occurs as vitreous, dark-brown to black, metamict grains and as black inclusions. The inclusions are generally irregular in shape and hardly visible in samples under microscope. The BSE image and the chart of the analyzed uraninite grains showed in Fig. 4A.

Pitchblende (Triuranium octoxide ($UO_{2.67} = U_3O_8$))

The most common uranium oxides in nature are the triuranium octoxide (U_3O_8) and uranium dioxide (UO_2). Both of them are solids with low solubility in water and stability over a wide range of different chemical/environmental conditions [8]. According to [11], the composition of uraninite ideally is UO_2 . U= 46.5% to 88.2%. Normally U^{4+} is oxidized to U^{6+} to a varying extent. As the U^{4+} ion is replaced by the smaller U^{6+} ion, extra O ions enter to occupy interstitial positions ($UO_{2.67} = U_3O_8$). Triuranium octoxide occurs in the form of minute disseminated particles associated with the other primary uranium minerals and pyrite in carbonaceous shale bearing sandy-dolostone. It ranges in color, from greenish black with a typical conchoidal fracture to a grayish black or black variety. The small size of the triuranium octoxide does not allow detection by a separate XRD pattern. Fig. 3C shows Pitchblende (triuranium octoxide) associated with magnetite.

Uraninite has been synthesized between 50 and 212°C by reduction of uranyl ions by H_2S or Fe^{2+} , and by organic liquids at room temperature [12]. In this study, grains were investigated by the ESEM technique (Fig. 4A), that show the crystals contain a variable average content of U percent that fluctuated between 74.3% and 92.6% in different samples. Figure 4 shows that the crystals contain Pb up to 2.4%, and that the Si percent fluctuated between 0.3% and 3.6% in different samples. Uraninite compositions in the samples are never uniform; they vary not only from grain to grain, but even at the microscopic level within the same uraninite grains.

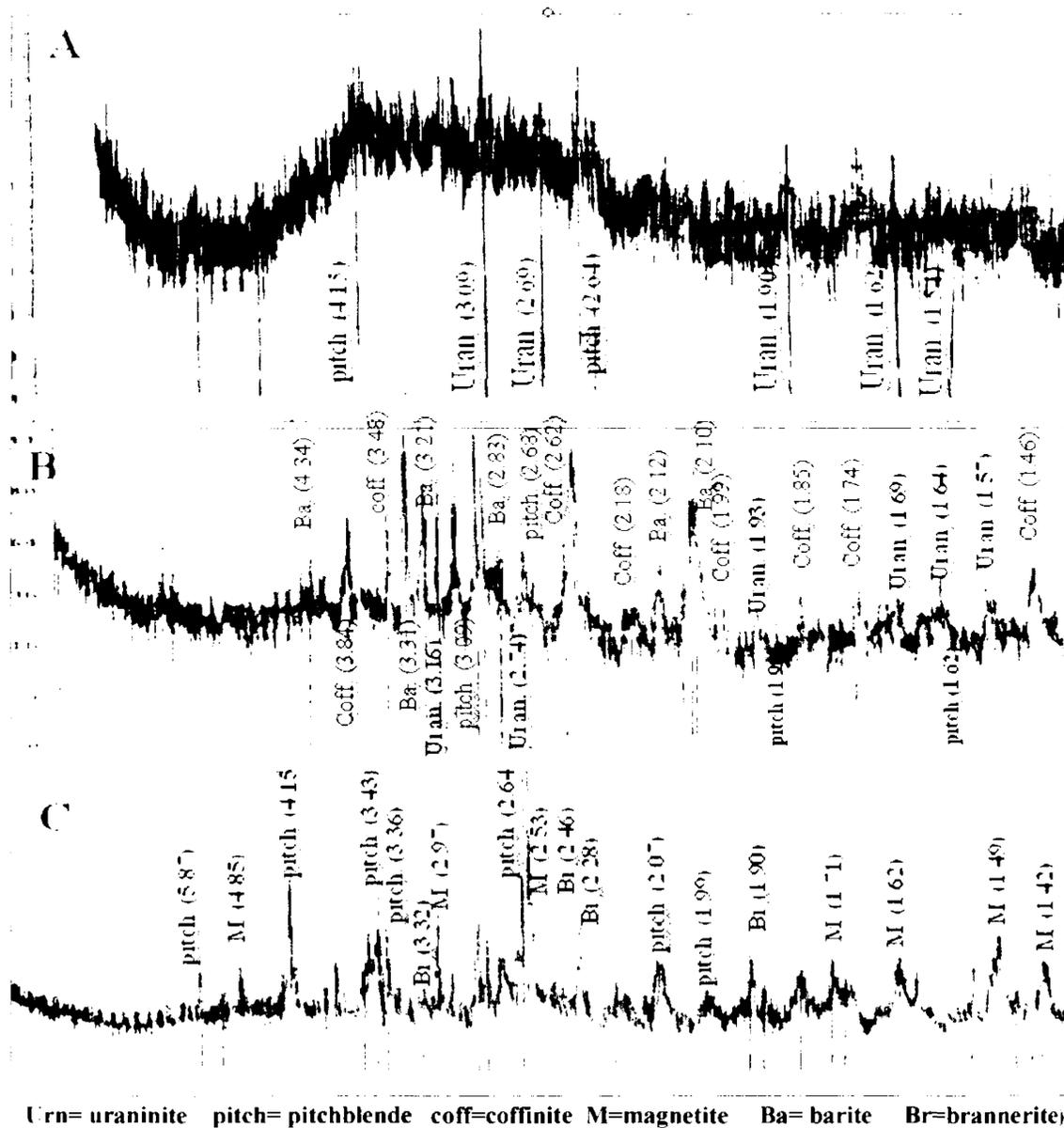


Fig. 3. XRD pattern of A- B- uraninite (UO_2) C- Pitchblende (U_3O_8).
Coffinite (USiO_4)

Coffinite has been found as minute grains in numerous anomalous spots located within the carbonaceous materials. The hand picked grains were examined by both Scanning electron microscope (SEM) Fig. 4B. and XRD. Figure 5 shows the XRD pattern of the investigated grains where the coffinite is generally associated with magnetite and hematite. The ESEM examination of the coffinite grains (Fig. 4B) shows the possibility of uraninite being replaced by coffinite and the latter surrounded by quartz. This indicates that uraninite has been subjected to some degree of coffinitization.

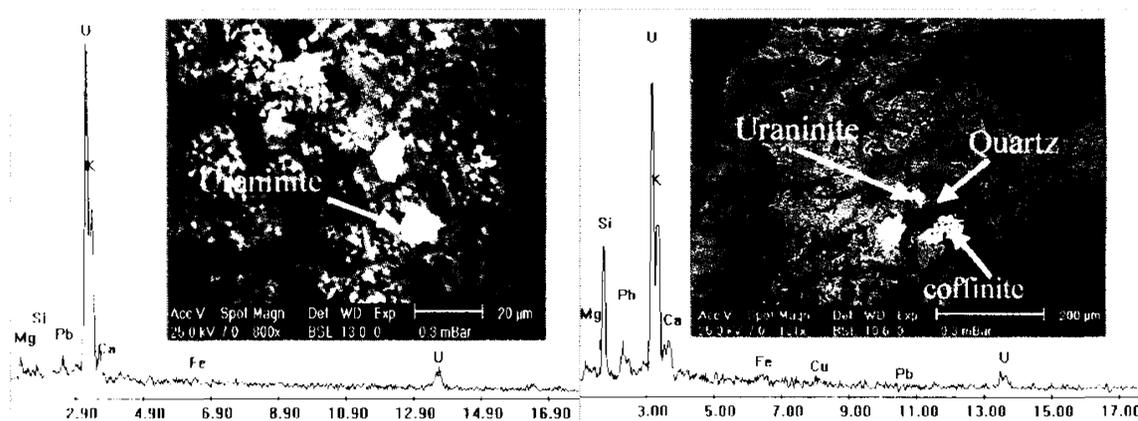


Fig. 4. BSE image and the chart of the analyzed A- uraninite mineral and B- coffinite associated with uraninite and quartz.

Coffinitization seems closely associated with uraninite and quartz when these closely coexist with pyrite and organic matter. This agrees with [13], who indicated that coffinitization can take place most likely at temperatures below 130°C if dissolved silica concentrations are limited by an amorphous silica mineral phase. Redox condition and silica concentration have been considered as two major factors controlling coffinite formation. Coffinitization of uraninite has been generally considered to take place in a relatively reducing and silica-rich environment [14a&b]. Coffinite thus occurs as reaction rims between uraninite and quartz grains (Fig. 4B).

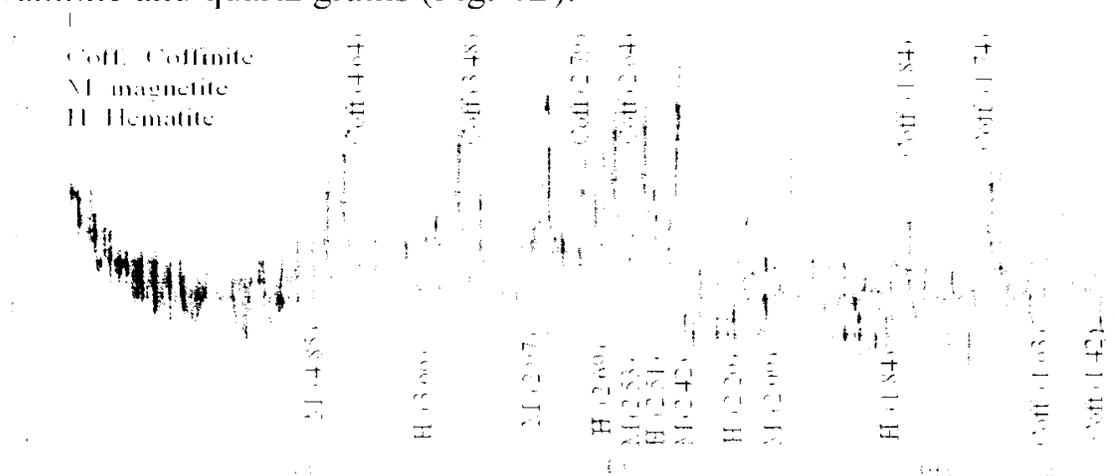


Fig. 5. XRD pattern of coffinite associated with iron oxide minerals.

Secondary uranium minerals: The secondary uranium minerals are observed in zones with variegated colors where greenish-yellow, pale yellow and yellowish-red colors are predominant. The examined grains

show the presence of sklodowskite, torbernite and uranophane as will be described below.

Sklodowskite $[\text{Mg}(\text{UO}_2)(\text{SiO}_3\text{OH})_2(\text{H}_2\text{O})_6]$ is a hydrous magnesium uranyl silicate hydroxide mineral. It occurs as disseminations scattered through the oxidation zone. The minerals were identified using XRD and confirmed by using the ESEM technique (Fig. 6A).

Torbernite $[\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}]$ is the most common secondary uranium mineral in the Allouga area, and may be associated with uranophane in the uppermost part of the oxidation zone. Torbernite was observed in cavities as individual, bright green, transparent to translucent, tabular mineral and as leaf-shaped crystals (Fig. 6B).

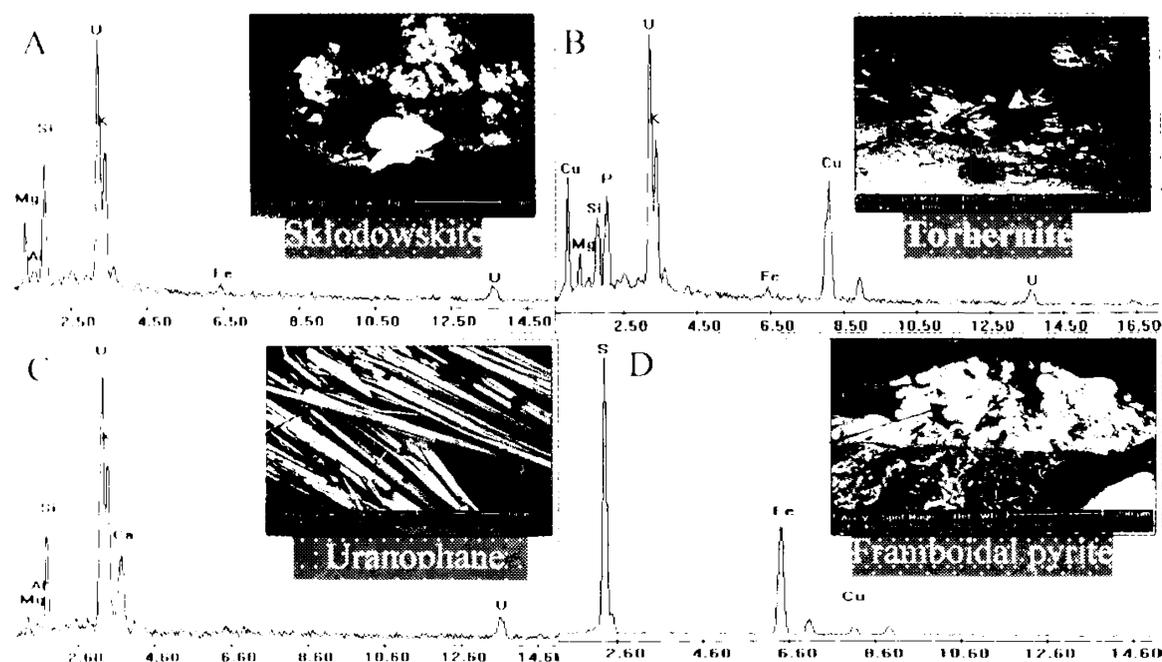


Fig.6. BSE images and the charts of the analysed grains of A- Sklodowskite B- Torbernite C- Uranophane and D- Framboidal pyrite.

Uranophane $(\text{Ca}(\text{UO}_2)_2\text{SiO}_3)$ is much rarer than sklodowskite and torbernite in the Allouga area and has a straw-yellow color and is found mostly as fibrous radiating aggregates. Uranophane is found in fissures as coatings on a surface, where it is intergrown with copper minerals. It also forms as aggregates of needle-shaped crystals (Fig. 6C).

Paleochannel concept and uranium minerals paragenesis.

The uranium mineralization at Allouga is hosted in the carbonaceous shale-bearing sandy-dolostone forming parts of the Um Bogma Fm. Uranium is concentrated along many local normal faults striking NNW-SSE in areas where organic matter and framboidal pyrite are present (Fig. 6D).

At the end of the Lower Carboniferous, the post-Visean uplifting was accompanied by E–W fault systems and affected a large part of the NE African plate. As a result, most of the pre-Visean deposits were eroded from uplifted areas [15]. The Um Bogma Formation was mostly precipitated in a shallow marine environment. After deposition of the lower massive dolostone member, a period of intense rainfall prevailed, leading to the formation of caves (karstification), channels, lagoons and marginal basins. This period was followed by arid to semi-arid climatic conditions, resulting in evaporates and accompanied by intensive weathering and erosion leading to the formation of fluvial and lacustrine deposits. These deposits filled the earlier channels, lagoons and basins to produce the paleochannels. This concept is substantiated by the presence of carbonaceous shale, rounded dolostone remnants, and several sandstone fragments within those channels.

The present explanation of the paleochannels mostly conforms to the views of [16] who define paleochannels as remnants of river and stream channels that have been filled with sediments and overlain by younger units. The environment was reducing, as illustrated by the presence of sulfides and carbonaceous materials. Accordingly, a redox zone is developed and can be located at the interface between the oxidation and reduction zones (Fig.7). The Um Bogma Formation was later subjected to tectonic processes, producing small-scale faults that acting as pathways for uranium-bearing circulating water. The uranium distribution (mobilized from pre-existing source and surrounding granitic rocks) largely follows these fractures and precipitated with carbonized matter. Uranium concentration is epigenetic, resulting from precipitation along both paleochannels and tectonic structures that contained as a redox boundary, especially at the margins of the paleochannels which contained carbonized matter (Fig.7).

The reduced material in the Allouga quarry contains coffinite and uraninite, which are typically intimately mixed with a carbonaceous matter, pyrite, barite and carbonate minerals. The ore body is partly oxidized at the top for about 5m. The oxidized zone contains a large variety of hexavalent uranium minerals, including torbernite, uranophane and sklodowskite. [3] Referred to the presence of *Desulfovibrio* sp. bacteria where they could separate this type of bacteria from carboniferous shale. This type of sulfate-reducing bacteria (*Desulfovibrio* sp.) is known to enzymatically reduce U^{6+} to U^{4+} and can grow using uranium as the sole electron acceptor [17]. The presence of this type of bacteria led to the deposition of U^{4+} -bearing

minerals as uraninite (triuranium octoxide) and coffinite in the redox state in the Allouga area.

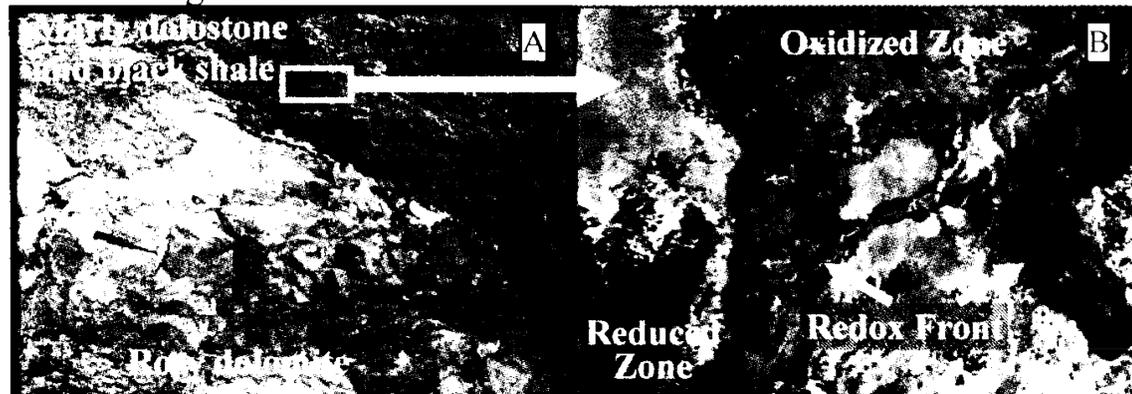


Fig.7. Margins of Allouga paleochannels with wavy surfaces containing carbonized matter that is considered to be a redox boundary.

Conclusion

The precipitation processes of uranium mineralization at the Allouga quarry were mostly controlled by; 1) gently-dipping, small-scale structures such as faults and joints which acted as pathways for U-bearing solutions to precipitate uranium at the most favorable sites, 2) the presence of carbonaceous matter and pyrite in reducing environments that resulted in the formation of the primary uranium mineralization of uraninite pitchblende and coffinite, 3) the presence of uraniferous granites, may be considered to be the main source of uranium, and 4) the presence of *Desulfovibrio* sp. bacteria which are known to enzymatically reduce U^{6+} to U^{4+} and help in the precipitation of the primary uranium minerals coffinite and uraninite.

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