CONTRIBUTION TO THE ORIGIN OF THE SYNGENETIC URANIUM ENRICHMENT IN THE EARLY MIOCENE CARBONATES OF THE EUPHRATES FORMATION, IRAQ

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ABSTRACT

A model is presented in this paper to account for various genetic aspects related to the origin and mode of formation of the so-called "syngenetic" uranium mineralization in the upper parts of the Euphrates Formation (Early Miocene).The proposed model considers the thick uraniferous Paleozoic clastic rocks as source rocks, lying several kilometers underneath. The late Early Miocene tectonic unrest triggered fracturing and faulting that allowed for uranium–rich groundwater, trapped in the Paleozoic aquifers, to ascend to surface in the shallow parts of the late Early Miocene Sea, together with bitumen and H_2S seepages. Uranium was precipitated in the interstitial pore environment, below sediment–water interface, where carbonate ion concentration was low, (following the precipitation of lime mud), uranium concentration was high and strong reductants were available (bitumen and H_2S). Short–lived tectonically–induced regressive phases led to episodes of emergence in the pertidal environment, which caused significant increase in the uranium concentration in the pore water environment leading to thin horizons of anomalous uranium concentration superimposed on a generally higher than background uraniferous carbonates. Early diagenetic dolomitization trapped the uranium, as urano–organic phases or cryptocrystalline pitchblend, inside the minute dolomite crystals, which generally kept them from oxidation and remobilization.

مساهمة في فهم أصل الإغناء الأولي باليورانيوم في الصخور الكاربونيتية لتكوين الفرات (المايوسين المبكر)، العراق

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المستخلص

تتناول هذه الورقة الظروف التكوينية لرواسب اليورانيوم أولية المنشأ في الجزء العلوي من تكوين الفرات (المايوسين المبكر). تتمثل الصخور المصدرية بفتاتيات تكوينات الدهر القديم السميكة والغنية باليورانيوم والواقعة بعمق عدة كيلومترات تحت سطح الأرض في المنطقة. ساهمت الحركات البنيوية التي حدثت في نهايات عصر المايوسين المبكر في إحداث صدوع إقليمية وتكسرات سمحت للمياه الجوفية الغنية باليورانيوم المحصورة في خزانات صخور الدهر القديم بالصعود إلى الأعلى وإغناء المناطق الضحلة من بحر المايوسين المبكر باليورانيوم فضلاً عن نقلها للقير وغاز كبريتيد الهيدروجين. ترسب اليورانيوم في بيئة الفجوات البينية ضمن رواسب الطين الجيري تحت سطح التماس بين الرواسب ومياه البحر حيث كان تركيز ايون الكاربونات واطىء بفعل ترسيب الجير الذي أدى بدوره إلى زيادة تركيز اليورانيوم في المحاليل البينية فضلاً عن وجود عوامل اختزالية قوية هي كبريتيد الهيدروجين والقير. عملت حركات بنيوية متعاقبة على إحداث دورات قصيرة الأجل من الإنحسار البحري حيث تكشفت الأجزاء الضحلة من حوض الترسيب المتأثرة بعمليات المد والجزر لفترات قصيرة وعمل

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التبخر على زيادة تركيز اليورانيوم في البيئات البينية ضمن رواسب الطين الجيري وترسيب اليورانيوم بكميات عالية أدت إلى نشوء طبقات ورقائق نحيفة غنية باليورانيوم أعلى من الخلفية الإعتيادية. ساهمت العمليات التحويرية المبكرة على احتجاز الأطوار الصلبة لليورانيوم المترسب ضمن بلورات الدولومايت الصغيرة على شكل معقدات عضوية أو على شكل بج بلند خفي التبلور مما عمل بشكل عام على حفظ هذه الرواسب من التأكسد واليورانيوم من الحركة والهجرة .

INTRODUCTION

The limestone of the upper part of the Euphrates Formation (Early Miocene) is characterized by anomalous uranium concentrations in most of the exposures and shallow subsurface sections along the Euphrates River. Two genetically different types of uranium enrichment were identified in these rocks; "syngenetic" and epigenetic. The latter is younger and was developed by the remobilization of uranium from the older uranium–rich carbonate horizons lying underneath (A1-Atia and Mahdi, 2005). This paper is concerned with the so–called "syngenetic" uranium enrichment in the carbonates of the Euphrates Formation.

Reports on uranium exploration in Iraq are numerous and cover wide areas, including field checking of all surface anomalies identified by radiometric airborne survey. However, some localities received more attention than others, such as Al-Qaim area (A1-Fadhli and Abdul Qadir, 1969 a and b, Al-Ani, 1977 and Abdul Qadir and Jassim, 1985, among others) and Abu Skhair (Hussain, 1980, Al-Atia et al., 1984 and Mahdi and Al-Hamad, 1986, among others). Exploration work was also conducted in Taqtaqana (Al-Kazzaz and Mahdi, 1991), Shithatha and Hit (Al-Atia et al., 1977 and 1979), Hit (Abass and Sadalla, 1984).

Despite the high number of investigators, the problem of uranium genesis is seldom tackled in the previous works. Among the pioneer works in this respect is that of Al-Fadhli and Abdul Qadir, (1969 a and b) on the genesis of Al-Qaim epigenetic uranium deposits, which was also discussed by Al-Ani (1977). They suggested the exposed Cretaceous and Tertiary phosphorites as a source of uranium and groundwater, as transporting agent.

A genetic model was presented by Al-Atia et al. (1977) on the uranium showings of Hit and Shithatha areas, where a hydrothermal origin related to the basement complex was speculated. Al-Kazzaz and Hussain (1977) thought that deep acidic magma may be involved. Whereas Al-Kazzaz and Mahdi (1991) suggested the presence of two types of uranium deposits; a syngenetic and an epigenetic uranium mineralization. The uranium in the former was precipitated from uranium – rich sea water (source not identified) and in the latter uranium was leached and mobilized from the syngenetic type by groundwater action to be precipitated as secondary yellow uranium – minerals in the Brecciated Unit and in the clayey green unit of the Euphrates Formation.

Recently, Al-Atia and Mahdi (2005) discussed the origin of the epigenetic uranium mineralization at Abu-Skhair deposit and suggested leaching groundwater and upward migration of uranium from the epigenetic

uranium–bearing dolomite horizons in the upper parts of the Euphrates Formation and redeposition in swamp deposits at the contact of the Euphrates Formation with the overlying units.

THE EUPHRATES FORMATION

The Euphrates Formation consists of marine carbonate rocks throughout. It has wide exposures on the southern and western sides of the Euphrates River. It extends from Al-Qaim in the NW to Samawa in the SE, where it interfingers with and passes laterally to Ghar Formation (Fig. 1). The formation was divided into three units: A, B and C, from older to younger (Al-Mubark, 1974). Uranium mineralization is shown in Unit C only, which is the most wide spread unit of the Euphrates Formation in the desert area. It is composed of 25m soft, fossiliferous, bluish green marl interbedded with thin beds of shelly recrystallized limestone or oolitic shelly limestone. It varies in thickness from 10 m (in Haditha area) to 22 m (in Wadi Ghdaf) and up to 30 m (in Anah area) . Part of the so – called Unit C was recently included in the Nfayil Formation (Sissakian, 2000).

Petrographically the Euphrates Formation consists of bio – dolomicrosparite and calcareous dolostone in the lower parts and dolomitic algal biosparite, coarse crystalline fossiliferous limestone, biosparite, oolitic biopelsparite and sandy biodismicrite, in the upper parts (Al-Hasani, 1973 and Yass, 1980).

Bituminous matter, clay and pyrite are found in the aphano and very fine crystalline dolomites of Unit C. The bituminous matter is found in dolomicrite in two forms: scattered patches and as coating of fossil shells and pellets (Abdul Latif, 1986). Evidence of vanished evaporites and sabkha environment were presented by Abdul Latif (1986) based on her pertorgraphic study of uraniferous carbonates of the Euphrates Formation in Abu Skhair deposit.

Based on faunal evidence, the carbonates were deposited in warm tropical to subtropical shallow marine environment. Unit C, in particular, represents sedimentation in quiet, warm and shallow marine conditions (0 – 50) m deep. Evidence of reducing conditions were mentioned by Abdul Latif (1986). This quiet character of sedimentation was interrupted, according to Jassim et al. (1984), by active, very shallow marine conditions indicated by the shelly horizons. Hassan et al. (2002) found that brecciation and undulation in Unit C are expressions of synsedimentary episodes of tectonic unrest in the late Early Miocene.

THE EUPHRATES FAULT ZONE

The Euphrates Fault Zone has clear surface expression, (physiographic expressions) such as linear cliffs, especially in its southern extension .In the northern part it was well defined in subsurface by seismic reflections (Fouad, 2004).

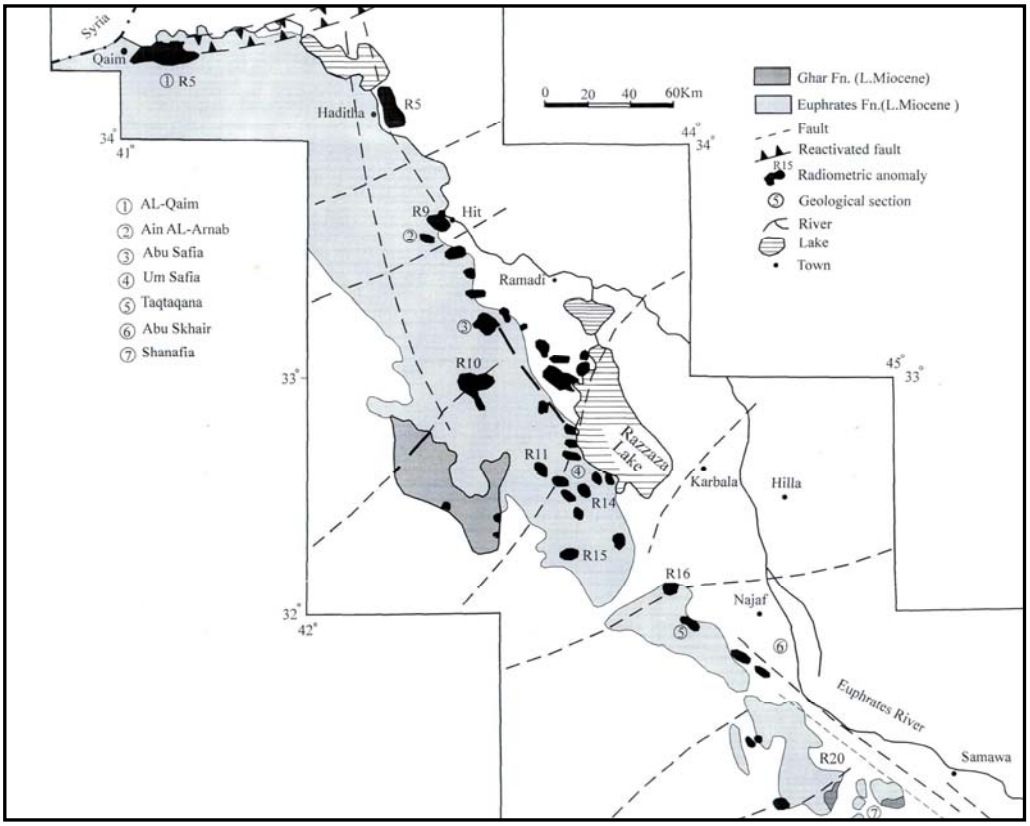

Fig. 1: Geological , structural and radiometric map west of the Euphrates River (Compiled from: Buday and Jassim, 1984, Jassim et al., 1986, Fouad et al., 1986 and C.G.G., 1974)

It consists of a system of faults making a fault zone in the Hit – Abu Jir area, with strike slip general character evidenced by pressure ridges and sag ponds on surface and the presence of positive and negative flower structures in subsurface (Fouad, 2004). In the Anah – Al-Qaim area these faults are related to the evolution of the Anah graben .They were reactivated during the inversion of the Anah graben in the Miocene. The age of the Euphrates Fault Zone is believed to be Campanian associated with an extension phase that affected the interior of the Arabian Plate, at that time. However, it was reactivated in the Early Miocene (Fouad, 2004).

Evidence of the Early Miocene rejuvenation of the Euphrates Fault Zone can be seen as episodes of synsedimentary tectonic disturbance reflected by brecciated and /or undulated horizons and slump structures in the upper parts of Unit C of the

Euphrates Formation (Fouad et al., 1986 and Hassan et al., 2002). This tectonic disturbance was noticed much earlier by Bolton (1954). He mentioned that towards the end of the Early Miocene, earth movements brought about radical geographical changes which terminated the period of quiescent deposition. He added that in some localities fracturing and faulting occurred, which allowed the eruption of bituminous mineral springs and gas seepages, which built themselves up into sinter – cones composed of bitumen and travertine. Bolton (1954) suggested the possibility of earthquakes triggering the slumping processes and possibly enhancing gaseous escape in the late Early Miocene.

SUBSURFACE GEOLOGY

Some deep wells were drilled in the area for oil exploration. AKK–1 was drilled in the Al-Qaim area (T.D. 4258m) and West Kifil–1 was drilled in the Abu Skhair area (T.D. 5872m). The former reached the Cambro – Ordovician unit (Khabour Formation) and showed thick Paleozoic units of Silurian age (Akkas Formation),Upper Devonian – Early Carboniferous (Perispiki , Chalki , Keista , Ora and Harur Formations) and Upper Carboniferous – Early Permian (Ga'ara Formation). The Upper and Middle Devonian units are missing in this well.

West Kifil–1 well was stopped at the Upper Carboniferous – Early Permian unit (Ga'ara Formation).Sandstone and shale dominate the lithology of these Paleozoic rock units. They show great thicknesses (Table 1). Basement depth was estimated on the basis of aeromagnetic results by about 10 Km along the Euphrates River basin; ranging from 7 Km, in the Anah area to 12 Km, in the Ramadi region (C.G.G., 1974).

Table 1: Thickness of Paleozoic rock units in subsurface sections (reported in Al-Qwaizi, 1997)

Cycle	Paleozoic units	Thickness (m)
Late Carboniferous – Early Permian	Sandstone with shale alternation	72 – 854
Late Devonian – Early Carboniferous	Sandstone with limestone	358 – 746
Silurian	Upper shale Lower shale (hot shale)	745 118
Ordovician	Upper sandstone Upper shale Lower sandstone Lower shale	135 610 134 1035

Samples from the Paleozoic units in several deep oil and groundwater exploration wells (AKK–1, Khlesia –1, KH 5/1, West Kifil–1 and Atshan –1) were analysed for uranium by Al-Qwaizi (1997). He found that most of these Paleozioc units are radioactive with respect to uranium (Table 2). The results show that uranium content ranges from (45 – 84) ppm in these units, believed to be either associated with zircon (in the sandstones) or with organic matter (in the shales) (Al-Qwaizi, 1997). The overlying Mesozoic and Tertiary units are mostly carbonates of marine origin with some phosphate and shale horizons in the Upper Cretaceous units in the sections described in Anah Graben (Al-Haza'a, 2001).

Table 2: Concentration of uranium in the Paleozoic rock units (Al-Qwaizi , 1997)

Unit	Range U (ppm)	Mean U (ppm)	Well No.
Ordovician sandstone	35 – 105	64	AKK–1
Ordovician shale	23 – 76	45	AKK–1 & Khlesia –1
Silurian black shale (hot shale)	46 – 124	78	AKK–1 & Khlesia –1
Permocarboniferous sandstone	71 – 99	84	West Kifil – 1

GROUNDWATER

The Euphrates Fault Zone is characterized by numerous mineral springs associated with H_2S and occasionally with bitumen. They are located along faults and lineaments. Two types of water were recognized (Mahdi et al., 2005). A sulfatic type rich in uranium (10 – 250) ppb, believed to be flowing from relatively shallow aquifers of the Euphrates and Dammam Formations. The other type is a chloride type, rich in Ra and some base metals (such as Zn, Hg, Pb, Cu and Mo) with little uranium content (0.1 ppb) and believed to be of deeper sources; probably associated with deep hydrocarbon accumulations. Water salinity is low to moderate, ranging from (500 – 5000) ppm in both types and the temperature ranges from (27 – 34) ^{o}C in the chloride type and (15 – 22) ^{o}C in the sulfate type (Al-Atia et al., 1977). The associated bitumen is rich in Ra rather than uranium.

URANIUM MINERALIZATION

The aerospectrometric survey of Iraq (C.G.G., 1974) showed consistent and semi continuous belt of radioactive anomalies along the Euphrates River basin and mostly at the southern and western sides of the basin (Fig. 1 and Table 3). These radioactive anomalies were attributed to uranium mineralization by the

C.G.G. (1974). They coincide on surface with two geological features. They are mostly related to the exposures of the Euphrates Formation, on one hand , and with the Euphrates Fault Zone on the other hand .The latter consists of two parts; a NW–SE trending fault zone (Hit –Abu Jir Fault System) and an E – W trending fault (Anah Fault) (Fig .1).

Table 3: Intensity of radiometric anomalies along the Euphrates Fault Zone (C.G.G., 1974) (See Fig. 1)

Anomaly No.	Source	Intensity (count/sec)
R5	U	200 – 300
R9	U	400 – 6800
R10	U	600
R11	U	400 – 1200
R14	U	300 – 400
R15	U	400
R16	U	250
R25	U	250 – 400

More than three decades of geological investigations have shown that the upper parts of the Euphrates Formation (top of Unit C) is characterized by generally higher than normal uranium concentrations (more than 10 ppm U) and by the presence of (2 – 3) thin horizons of higher radioactivity with uranium concentration reaching up to 300 ppm (Al-Kazzaz and Mahdi,1991). These radioactive horizons were encountered in most of the exposures and near–surface sections of the Euphrates Formation, from Al-Qaim in the northwest to Nassirriya in the southeast (Fig. 2).

The uranium concentration in these horizons generally ranges from (10 – 300) ppm, (mean about 80 ppm). The host rocks are mostly dolostones, white, gray pale brown and yellow in color, tough, occasionally fossiliferous and clayey, commonly contain organic or bituminous matters (Abdul Latif, 1986). The thickness of the uranium–bearing horizons average about 30 cm, each .They are persistent and show regional extension along the western side of the Euphrates River. No definite uranium minerals were identified, but many workers believe that uranium is trapped inside the dolomite crystals in some unidentified form (Al-Fadhly et al., 1969 a, Al-Ani, 1977 and Al-Kazzaz and Mahdi, 1991). Secondary (epigenetic) uranium deposits were developed in certain localities, such as Al-Qaim and Abu Skhair. Uranium was oxidized and leached from the "syngenetic" uranium–bearing horizons lying underneath and redeposited near the erosional contact of the Euphrates Formation with the overlying units (Al-Atia and Mahdi, 2005).

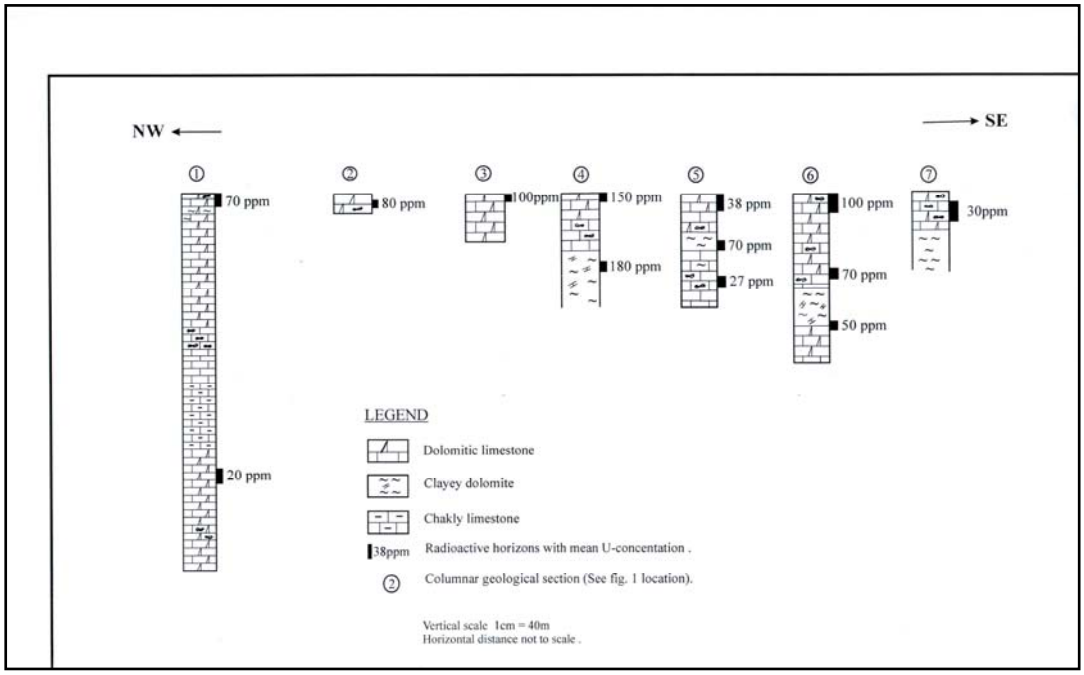

Fig. 2: Columnar geological sections of the radioactive part of the Euphrates Formation (Early Miocene)

EQUILIBERIUM STATE OF URANIUM

The state of the uranium equilibrium relative to its daughters was studied in hundreds of samples in almost all of the uranium deposits and showings in the Euphrates Formation. The data were gathered and discussed by Al-Kazzaz and Mahdi (1991). The samples analyzed represent a mixture of "syngenetic" and epigenetic mineralization in most of the localities, except in Abu Skhair and Al-Qaim, where clear distinction was made.

The results show that uranium in the so – called "syngenetic" mineralization, usually found in thin dolostone horizons, is in equilibrium state in about 60 % of the samples in Abu Skhair and in 31% in Al-Qaim. The rest of the samples show disequilibrium in favour of uranium. On the other hand, the epigenetic uranium mineralization in these two localities show that the equilibrium state is in favour of uranium in 90 % of the samples in Abu Skhair and in (26 – 99) % in Al-Qaim. Whereas, samples showing equilibrium state range from about (1 – 10) % only. Samples from Shithatha and Taqtaqana show that about 27 % of the samples are in equilibrium state and about 62 % in favour of uranium (epigenetic). Disequilibrium in favour of Ra was noticed in the Brecciated (porous and permeable) Unit of the Euphrates Formation as in Al-Qaim area (Table 4).

Table 4: Equilibrium state of uranium in the Euphrates Formation
(Data from Al-Kazzaz and Mahdi, 1991)

State of equilibrium	Rocks Type			Area
	Dolomite %	Breccia %	Clay %	
Disequilibrium in favour of U	52	26	99.5	Al- Qaim
Disequilibrium in favour of eU	17	57	0.0	
Equilibrium state	31	17	0.5	
Number of samples	125	520	118	
Disequilibrium in favour of U	63			Shithatha
Disequilibrium in favour of eU	9			
Equilibrium state	28			
Number of samples	162			
Disequilibrium in favour of U	61.8			Tagtaqana
Disequilibrium in favour of eU	10.5			
Equilibrium state	27.6			
Number of samples	140			
Disequilibrium in favour of U	40			Abu Skhair "syngenetic"
Equilibrium state	60			
Number of samples	500			
Disequilibrium in favour of U	90			Abu Skhair "epigenetic"
Number of samples	950			

DISCUSSION

Uranium ores are not commonly found associated with limestone or dolostone. A few occurrences were reported in New Mexico and Wyoming (USA) and in Bakouma (Central Africa).Uranium in calcrete deposits was reported in Australia, Namibia and Somalia (Adler, 1974).

All the reported uranium deposits in carbonate host rocks are epigenetic. Non have been reported as syngenetic so far. The enrichment of water with carbonate and bicarbonate anionic groups keeps the uranyl ion in solution, where uranly complexing with carbonate ions in water keeps it in a soluble form (Dall'aglio et al., 1974). The occurrence of "syngenetic" uranium deposits in the carbonates of Euphrates Formation seems to be unique at the present state of knowledge. Several theories have been put forward to explain the phenomena of uranium mineralization in the Euphrates Formation. A discussion of these ideas will be presented here.

Exposed phosphate rocks as a source of uranium

Two theories were presented in this respect .The earlier one was postulated by Al-Fadhli and Abdul Qadir, (1969 a) concerning Al-Qaim uranium deposit .However, they denied a syngenetic origin for these deposits on the basis of the following argument:

"Uranium could not have been precipitated syngenetically with the carbonate rocks due to the fact that the deposition of carbonate sediments occurs in oxidizing environments and because carbonate and bicarbonate ion concentration keep uranium ion; mostly $\{(UO_2)\ (CO_3)_3\}^{4-}$ dissociated in solution (Bell, 1963)". They argued about an epigenetic origin for Al-Qaim deposits. According to their hypothesis "uranium ion–bearing solution (pH about 7 – 8) was derived from the source area (uranium–bearing phosphate rocks of Rutba area) by mean of groundwater ".

Al-Fadhli and Abdul Qadir (1969 b) suggested that uranium was precipitated at and below the fluctuated paleo – water table within the pervious and semi–pervious rocks of the Euphrates Formation. This hypothesis probably explains, in part, the secondary (epigenetic) uranium mineralization in Al-Qaim area. At the time of the Miocene, the Upper Cretaceous and Early Tertirary phosphorites were exposed and since then went through weathering and erosion. These phosphorites contain about (50 – 100) ppm uranium, which is typical of this type of sedimentary marine phosphorites (Al-Bassam, 1982). Uranium can be oxidized, leached and mobilized until reprecipitated again in suitable host rocks.

However, this theory does not explain why there is no secondary uranium showings in the other rock units, younger than the Euphrates Formation, such as Ghar, Nfayil and Zahra Formations, considering that the phosphorite source rocks are more exposed now than before and the groundwater movement is still with the general dip direction (from W to E and NE) (Araim ,1990) .

Furthermore, this hypothesis does not explain the other uranium showings along the Euphrates River basin, occurring strictly within the upper parts of the Euphrates Formation. Moreover, the Iraqi phosphorites are rich in vanadium (Al-Bassam et al., 1990) and in the presence of vanadium ions or ionic complexes, stable uranyl vanadates, such as carnotite and tyuyamunite are likely to form insitu and hinder further uranium mobilization (Adler,1974). These secondary yellow uranium minerals are very common in the phosphorite exposures of the Western Desert.

The other theory considering exposed marine phosphorites, as a source of uranium was presented by the co – authors of this paper (Mahdi and Al-Delaimi, 2005). They believe that upon exposure of these deposits in the Early Miocene, uranium was leached and mobilized by surface waters during wet periods via great rivers flowing from the west, where the phosphorites are exposed, towards

the shores of the Early Miocene Sea, in the east. Mahdi and Al-Delaimi (2005) also included the igneous rocks of the Arabian Shield as a possible source of uranium transported fluvially towards the Early Miocene Sea. Evidence of such rivers is suggested by the presence of sandstone facies (Ghar Formation) interfingering with the carbonates of the Euphrates Formation in the investigated locations (Fig. 3).

According to Mahdi and Al-Delaimi (2005) the fluvial transport of uranium led to the enrichment of the late Early Miocene Sea with dissolved uranium at certain episodes and upon change of water chemistry and pH by mixing of two water types (fluvial and marine), uranium was deposited sygenetically together with the carbonates. Clayey and organic – phosphatic materials worked, according to Mahdi and Al-Delaimi (2005), as reductants of uranium and helped in its syngenetic precipitation in abnormal concentrations.

This theory differs from the previous one in several points. Firstly, it suggests surface water as transporting agent, secondly it deals with the syngenetic mineralization of uranium and thirdly it argues for an enrichment of uranium in sea water. However, it does not explain why uranium was concentrated in specific horizons, which have regional extension, and does not solve the problem of simultaneous deposition of uranium with carbonates, which is a geochemical barrier. Moreover, it ignores the fact that phosphorites of the Western Desert and igneous rocks of the Arabian Shield continued as exposures after the Early Miocene, but without any uranium enrichment neither in the clastics of the Ghar Formation (Early Miocene) nor in the carbonates and clastics of the younger formations such as Nfayil, Injana, Ddibdibba and Zahra, all of which received clastics contribution (especially Dibdibba and Zahra) from the western plateau, where the suggested source rocks are exposed .

Subsurface magmatic igneous rocks as a source of uranium

This is a very interesting theory presented by Al-Atia et al. (1977) where a primary uranium source of magmatic origin close to the basement rocks was suggested. In this theory uranium was leached by hydrothermal solutions and travelled long distances upward, through fractures and faults. The dispersed uranium may have been trapped in certain horizons where favourable conditions for uranium accumulation existed. A uranium trap was speculated below bitumen accumulation in some areas such as Hit. The depth of the primary source of uranium was suggested by Al-Atia et al. (1977) to be about 3500 m, based on temperature of spring water and on thermal gradient. They considered spring water as of hydrothermal origin and they believed that uranium was transported by these waters and concentrated in a shallower, rich in hydrocarbon accumulation.

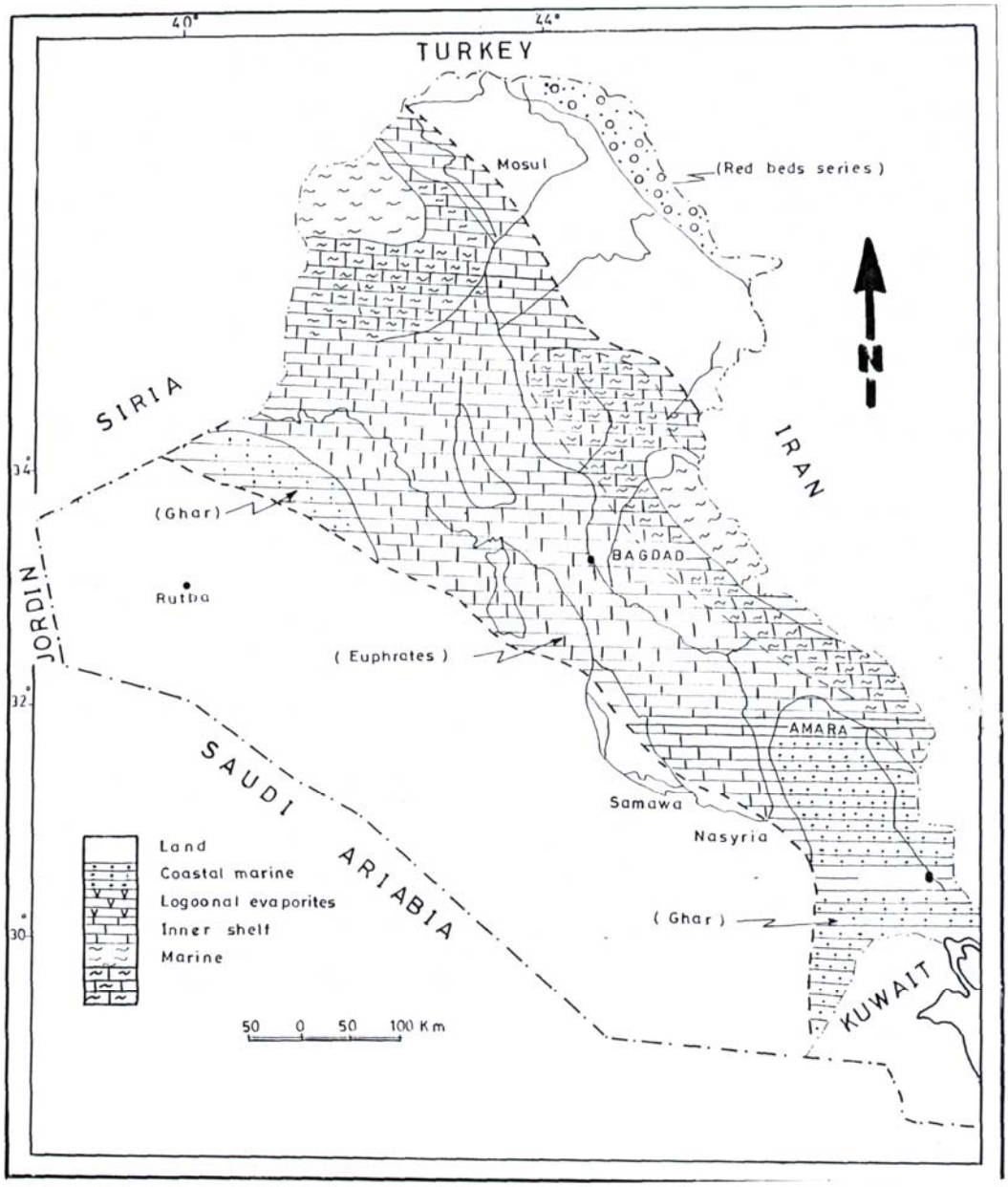

Fig. 3: Paleogeographical map of the Early Miocene (Jassim and Karim, 1984)

This theory was actually presented to explain the anomalous radiation in the Hit – Shithatha area. At that time many of the U – rich deposits along the Euphrates River basin were not investigated yet and the regional importance of

the Euphrates Formation as a uraniferous rock unit was not clear, at that time. Consequently, it does not tackle the subject of this paper, but it has presented new ideas for the first time relating faults, fracture zones, ascending thermal ground water and hydrocarbon subsurface accumulations in one model.

However, later studies by some of these authors (Al-Kazzaz and Mahdi, 1991) have denied such theory and went for unexplained syngenetic enrichment in the Early Miocene Sea. Others went for shallower sources of uranium to explain the epigenetic uranium mineralization in Abu Skhair (Al-Atia and Mahdi et al., 2005). They considered the primary uranium enrichment in the upper parts of the Euphrates Formation, as source for the richer accumulation of uranium in the uppermost parts of the formation. The recent work of Al-Atia and Mahdi (2005) and Mahdi et al. (2005) do not involve explanations for the syngenetic U–enrichment in the Euphrates Formation, but adequately explains the epigenetic U – enrichment at least in the Abu Skhair deposit.

THE PROPOSED MODEL

A regional phenomena such as the consistent uranium enrichment in a specific part of a rock unit extending as a belt for more than 1000 Km, requires a regional geological event to account for. The host rock, being of marine sedimentary origin, supports the idea of uranium enrichment in the Early Miocene Sea water, at the time of deposition, and the uranium equilibrium state suggests a syngenetic origin. The presence of several relatively thin horizons with anomalous uranium concentrations superimposed on a generally higher than background uraniferous unit, suggests short and repeated episodes of anomalous uranium precipitation controlled by regional factors .

The linear distribution of the uranium – rich zones along the Euphrates River basin and not all over the physiographic distribution of this formation requires controlling geological factors.The Euphrates Fault Zone, in its two parts: the Hit – Abu Jir – Nassirya and the Anah – Al-Qaim is the only linear geological feature that coincides, in space and time, with the distribution of uranium mineralization in the Early Miocene Euphrates Formation. The spatial distribution of the radiometric anomalies is in close association with surface expressions, as well as with subsurface extensions, of this fault zone (Fig. 1).

The Euphrates Fault Zone was reactivated in the late Early Miocene (Bolton, 1954, Jassim et al., 1984 and Fouad, 2004). The activation of this fault zone allowed for the first time the eruption of bituminous mineral springs and gas seepages along weakness zones. Bituminous travertine sinter cones are evidence of this activity (Bolton, 1954).

Evidence of the late Early Miocene unrest is shown in the undulations, slump structures and brecciation in the upper parts of the Euphrates Formation (Unit C) (Fouad et al., 1986 and Hassan et al., 2002). The Euphrates Faults are deep as

shown by seismic sections (Fouad, 2004) cutting through the basement, thick Paleozoic and much thinner Mesozoic and Cenozoic units. They allowed for groundwater (Na – Cl type) from deep aquifers to ascend through conduits to the surface since the Early Miocene (Bolton, 1954). These ground waters were and still are rich in H_2S and bitumen. Evidence of these seepages can be seen in travertine sinter cones and scattered patches of bituminous matter filling cavities or coating fossil shells and pellets in the upper parts of the Euphrates Formation (Abdul Latif,1986). The dark opaque zones inside the dolomite crystals may be related to residues of bituminous matter trapped inside these crystals in the early stages of diagenesis. At present, most of the springs along the Euphrates Fault Zone are bituminous and rich in dissolved H_2S.

Uranium equilibrium state in these waters is destroyed in favour of radium by the hydrogeological system (Al-Atia et al., 1977). The Euphrates Faults were important in the localization of the uranium mineralization in the Euphrates Formation. Their role was two folds: they retarded the natural flow of groundwater down dip and thus allowed uranium to be transported upwards via fault surfaces, conduits and fracture zones and to contaminate the Miocene Sea in the area of influence of these faults. They also allowed the seepage of reductants (H_2S and bitumen) to the depositional environment.

A deep uranium source of magmatic origin was speculated by Al-Atia et al. (1977). According to these authors, uranium was leached by hydrothermal fluids and travelled long distances through conduits along fault planes. In the present study we suggest the thick uranium – rich Paleozoic shales and sandstones as primary sources of uranium. The analysis reported by Al-Qwaizi (1997) shows anomalous concentrations of uranium in the clastics of Khabour, Akkas, Ora and Ga'ara Formations, in subsurface sections, in western and central Iraq. According to Al-Qwaizi (1997) uranium in these clastics is hosted by zircon or organic matter. However, results from older work by Yakta (1971), which were ascertained in this study, showed the Khabour Quartzite to be rich in phosphate grains (bones and intraclasts) which may account for part of the uranium present in these units. It is clear from the analysis reported in Al-Qwaizi (1997) that uranium and zircon concentrations are not proportional and suggest that zircon can not account for all the uranium present in these rocks. Zr / U ratio in zircon may vary from (200 – 3000) (Patchett and Jocelyn, 1979 and Ismail, 1996). In the Paleozoic units of the investigated sections this ratio is (3 – 6) only according to the analysis of Al-Qwaizi (1997), pointing towards multisources and hosts of uranium in these rocks including zircon and francolite in the sandstones and organic matter and clay minerals in the shales.

The Paleozoic sediments were laid down in these parts of Gondwana megacontinent in great sedimentary basins (Buday, 1980). In the Iraqi territory

these thick units are composed of several hundreds of meters of clastics (shales and sandstones). They have territorial extension, without great variation in thickness or lithology, from the Western Desert to Northern Thrust Zone. Full thicknesses are exposed in northern parts of Iraq, but only the uppermost part is exposed in the Western Desert. However, all deep wells drilled in western and central Iraq have penetrated these units or part of them (Al-Qwaizi, 1997). These units have a great potential for oil and gas and are rich in uranium.

The Paleozoic uraniferous shales and sandstones are suggested in the present study as a primary source of the syngenetic uranium enrichment in the late Early Miocene rocks as follow (Fig. 4):

During long history of diagenesis, uranium was leached from host minerals and materials such as francolite, zircon, clays and organic matter. Uranium was concentrated in the connate water. Significant volume of water is usually released during normal sediment compaction and diagenesis. The average shale is estimated to yield approximately 3.5×10^3 l of water during compaction for every $1m^3$ of solid deposited (Hanor, 1979).

Leaching of uranium from host minerals was probably enhanced by oxidizing and weakly acidic condition of diagenesis, brought about by exposure or by circulating oxygenated groundwater. Water in sand is dominated by Cl^- and tend to be slightly acidic (Hanor, 1979). Most of the stratigraphic records of the deep wells show a regional unconformity, where the Middle and Early Devonian rocks are missing (Baban, 1996, in Al-Qwaizi, 1997), which account for a time span of about 20 m.y. That is to say the Silurian and probably parts of the Ordovician rocks were exposed for weathering and oxidation for a long period of time, enhancing uranium oxidation and leaching.

Uranium–rich groundwater in the Paleozoic aquifers remained confined in the Mesozoic and early Tertiary times, flowing gently downdip, until the late Early Micocene unrest triggered its surface discharge through conduits developed by activation of deep faults, which retarded its normal down dip flow. Faulting of a sedimentary basin may provide a permeable conduit for the discharge of fluids from depth. These fluids will migrate upward when fluid pressure at depth exceeds hydrostatic pressure (Hanor, 1979). The same faults acted as conduits for hydrocarbons and associated H_2S seepages, which could have been trapped in the Jurassic sequence.

Uranium is possible to be transported in both oxygenated and deoxygenated ground water solutions (Adler, 1974). Faults and fracture zones undoubtely served as collecting points for H_2S and bitumen generated from hydrocarbon accumulation, which may represent dead oil left behind in a bleached or partially flushed oil trap (Backstorm, 1974). These weak zones provided easy access for the transfer of uranium from underlying sandstone and shale aquifers. Submerged groundwater seepages contributed to the relative enrichment of the shallow

bituminous matter. This enrichment was especially manifested where submarine seepages were active. In this shallow environment fine lime mud was precipitating, contaminated with bitumen and uranium ions. Uranium remaind in solution above sediment water interface as uranyl carbonate ion $[UO_2(CO_3)_3]^{4-}$ as long as the carbonate ion concentration was high. Uranyl complexing with carbonate ions in water keeps it in a soluble form, and is considered as the most

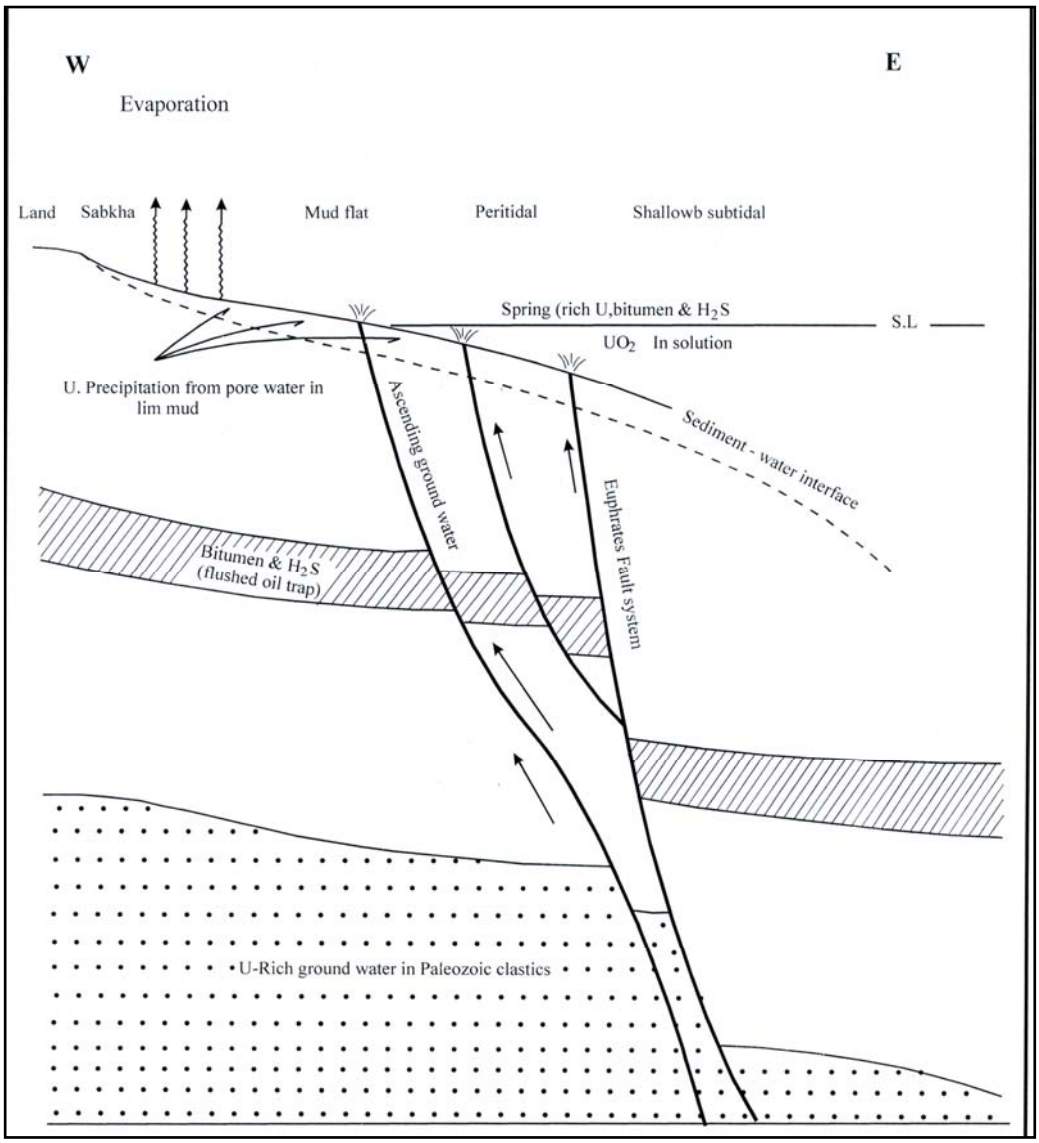

Fig. 4: Schematic diagram illustrating the proposed model of U – enrichment in the Early Miocene carbonates (not to scale)

effective uranyl chelating compound (Dall'aglio et al., 1974). However, below sediment – water interface high uranium concentrations were trapped, together with bituminous material in an H_2S – rich pore water of the interstitial environment in the unconsolidated lime mud.

The carbonate ion concentration in the pore environment should have been significantly lowered following the precipitation of carbonate and consequently the uranium concentration increased. In this interstitial micro – environment there were series of geochemical processes that have brought a very effective separation and concentration of uranium. The important geochemical process is the reaching of high UO_2 activity in pore water because of the low concentration or depletion of the carbonate ion. Furthermore, reducing conditions prevailed (H_2S and bitumen) evidenced by the common presence of pyrite (Abdul Latif, 1986). Since uranium can not remain in solution in neutral water (Kaplan et al., 1974), it precipitated intensively in the interstitial environment, especially in the presence of strong reductants, which can reduce U^{6+} to U^{4+} (Eargle and Weeks,1973). Reductants such as H_2S, petroleum humic acids and bitumen are capable or reacting with uranium in solution to bring about its precipitation (Adler, 1974). The generally above background uranium concentrations in the upper parts of the Euphrates Formation can be explained in this way.

Frequent shallowing events may have caused temporary emergence of the mudflats, evidenced by the presence of gypsum and vanished evaporites in some horizons (Abdul Latif, 1986), which periodically increased the concentration of uranium in the pore water by evaporation. These shallowing events may be related to tectonic pulses causing short regressive episodes that were repeated several times during the tectonically disturbed late Early Miocene time. These peculiar environmental conditions were able to cause, in a short time – range, intense uranium precipitation in relatively thin horizons, which were superimposed on a generally high uranium background in most of the tectonically disturbed upper parts of the Euphrates Formation.

Soon after the precipitation of the lime mud, early diagenetic dolomitization processes started in the mud flat environment. Uranium solid phases were trapped inside the minute dolomite crystals. The form of uranium is not confirmed yet, but it can be as urano – organic solids (W.G. 1, 1974) or as cryptocrystalline pitchblende. Neutral solutions of uranyl carbonates could react with H_2S to precipitate pitchblende at relatively low temperature (Miller, 1958; in Smith, 1974).

Burial and entrapment of uranium solid phases inside the minute dolomite crystals saved these uraniferous horizons from oxidation, leaching and mobilization. Exceptions occur where exposure and weathering under oxidizing conditions or leaching by highly oxygenated juvenile shallow groundwater, as it is the case in Abu Skhair deposit (Al-Atia and Mahdi, 2005).

Syngenetic uranium mineralization was never reported in the overlying rock units. Hence these uranium deposits are stratigraphically controlled by the upper part of the Euphrates Formation (Unit C). There is no solid evidence to explain why syngenetic uranium mineralization was not manifested in the younger rock units of this zone. However, according to the proposed model we can assume that the uranium – rich groundwater seepages from the Paleozoic aquifers were terminated by further tectonic pulses. Tectonic unrest continued after the Early Miocene in this zone until recent times (Sissaakian and Deikran, 1998). It can be assumed that the deep conduits, which penetrated the Paleozoic sequence, were blocked as a result of younger tectonic movement. However, H_2S and bitumen–rich groundwater seepages continued to be active, discharging from the shallower Jurassic aquifers.

CONCLUSIONS

A new model explaining the regional "syngenetic" uranium mineralization in the upper parts of the Euphrates Formation is presented in this paper. The following conclusions concerning various aspects of genesis are listed as follow:

- **Primary source rocks:** These are the thick Paleozoic sandstones and shales anomalously rich in uranium as shown by chemical analyses of samples collected from subsurface sections. Uranium was diagenetically released from host minerals into the formation connate water over millions of years of diagentic modifications.

- **Transporting agent and means of transport:** This is the groundwater ascending from the Paleozoic aquifers via fracture zones, fault surfaces and conduits triggered by tectonic unrest in the late Early Miocene. The groundwater was associated with H_2S and bitumen from flushed oil traps probably in Jurassic units.

- **Uranium precipitation:**This has taken place below sediment – water interface directly from pore water of unconsolidated sediments in mudflats and other peritidal shallow environments. Uranium precipitation was brought about by increased UO_2 activity, depletion of carbonate ion and presence of strong reductants H_2S and bitumen in the interstitial environment.

- **Uranium distribution:**The whole of the upper part of the Euphrates Formation was enriched with higher than normal background uranium concentrations. However, specific thin horizons are characterized by

remarkably high (anomalous) uranium concentrations. These can be related to tectonically enduced episodes of short – lived sea regressive phases, where evaporation in the temporarily emerged mudflats lead to the increase of uranium concentration in pore water and formation of uranium–rich horizons, superimposed on the generally high uranium background of the upper part of the Euphrates Formation.

- **Diagenesis and preservation:** Early dolomitization led to the entrapment of the uranium solid phases (possibly urano – organic phases and /or cryptocrystalline pitchblende) inside minute dolomite crystals. Crystal entrapment and burial preserved uranium from oxidation, leaching and mobilization, except in some parts where weathering destroyed the system.

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