

## URANIUM IN THE IRAQI PHOSPHORITES

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## ABSTRACT

The radioactivity of the marine sedimentary phosphorites of Iraq is investigated and found to be due to uranium. The Late Cretaceous – Early Tertiary phosphorite deposits are generally poor in uranium relative to other Tethyan deposits; they generally contain (20 – 50) ppm U and up to 100 ppm U in the francolite concentrates.

Strong positive correlation exists between uranium with  $P_2O_5$  and F. Most of uranium is believed to be present in the francolite structure as  $U^{4+}$  substituting for  $Ca^{2+}$ . Uranium in the Iraqi phosphorites seems to be generally in equilibrium with its daughter products with minor scattering around the equilibrium line. Secondary uranium minerals are found as metatyuyamunite in phosphorite and limestone, and as carnotite in shale.

It seems that the source of uranium is terrigenous, supplied by U-rich sandstones of older rock units and transported by rivers to shallow marine environments. Geochemical affinity of U towards phosphates and reducing conditions facilitated uranium incorporation in the francolite structure in the early stages of crystallization. The radioactivity of phosphorites provides excellent tool for surface and subsurface prospecting and exploration. But, the presence of uranium in the phosphate fertilizers represents an environmental hazard.

## اليورانيوم في الفوسفوريت العراقي

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## المستخلص

تبين هذه الورقة أن إشعاعية صخور الفوسفوريت الرسوبية البحرية في العراق تعود إلى وجود اليورانيوم وبشكل عام إن الرواسب الفوسفاتية الطباشيرية المتأخرة والثلاثية المبكرة فقيرة باليورانيوم قياساً على باقي رواسب التيثيس، حيث تحتوي الرواسب العراقية على (20 – 50) ppm من اليورانيوم ولغاية 100 ppm منه في ركاز الفرنكوليت. لوحظ وجود علاقة ارتباط موجبة قوية بين اليورانيوم و  $P_2O_5$  و F، ويعتقد أن معظم اليورانيوم موجود في تركيب الفرنكوليت البلوري بشكل ( $U^{4+}$ ) يحل محل ( $Ca^{2+}$ ). بينت هذه الدراسة أن هناك حالة توازن إشعاعي بشكل عام بين اليورانيوم وبناته مع وجود تبعثر قليل حول خط التوازن. وتبين وجود معادن ثانوية لليورانيوم هي الميتاتيامونيت ويظهر غالباً في الفوسفوريت والحجر الجيري والكارنوتيت ويظهر غالباً في السجيل. هناك دلائل على أن مصدر اليورانيوم قاري الأصل تم تزويده من الرمال الغنية باليورانيوم من التكوينات الأقدم ونقل بواسطة الأنهار إلى البيئات البحرية الضحلة وقد عملت الألفة الجيوكيميائية بين اليورانيوم والفوسفات والظروف الاختزالية على استيعاب اليورانيوم وتثبيتته داخل تركيب الفرنكوليت في المراحل المبكرة للتبلور. أن الخاصية الإشعاعية للفوسفوريت تتيح أداة ممتازة للاستكشاف والتنقيب السطحي وتحت السطحي غير أن وجود اليورانيوم في الأسمدة الفوسفاتية يشكل خطورة بيئية.

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## INTRODUCTION

All marine sedimentary phosphorites are radioactive. The radioactivity is mainly due to the presence of uranium; phosphorite is one of the most important uranium-bearing rock types in nature (Table 1). This criteria was used in surface and subsurface exploration for phosphorites with remarkable success in Turkey and Saudi Arabia (Sheldon, 1964 and 1967). Most marine phosphorites contain (0.005 – 0.02) % uranium, enough to be detected not only in gamma-ray well logs but also, under favorable circumstances, by aerial radiometric reconnaissance (Mckelvey, 1967).

Uranium content of phosphorites is variable (Table 2), and depends on several factors, including phosphorite facies, texture, weathering conditions, phosphorite content, diagenetic history, etc. Some phosphorite deposits are so rich in uranium that can be a uraniferous source. Uranium can be extracted, as a by-product, from phosphoric acid in the course of fertilizer production (Hurst and Crouse, 1973 and U.S. Atomic Energy Commission, 1949).

Several workers have discussed uranium in phosphorites from various points of view including geochemistry, mineralogy, crystal chemistry and extraction (Khalid and Abed, 1981; Altschuler *et al.*, 1958 and McConnell, 1973, among others). Many authors have considered this problem as part of their research work on the Iraqi phosphorites in general (Al-Bassam, 1974, Al-Dahan, 1977; Mohammad, 1985; Aba Hussain, 1987 and Al-Jaleel, 1983).

The previous workers have noticed a close positive relationship between  $P_2O_5$  and U concentrations and attributed this to the presence of uranium in the apatite structure. A study was made to show the use of gamma-logging in grade evaluation of some Iraqi phosphorites depending on the close association of gamma-intensity and phosphate concentration (Al-Bassam and Al-Bedaiwi, 1988).

Most of the data presented here are results of extensive work on the Late Cretaceous and Early Tertiary phosphorites of Iraq carried out by GEOSURV, Iraq (Al-Bassam *et al.*, 1990). Furthermore, results of postgraduate studies and available published work on the subject were also useful.

Table 1: Distribution of uranium in various rock types (ppm)  
(Hawkes and Webb, 1962)

Igneous rocks ( average)	2.6
Ultramafic	0.03
Mafic	0.8
Felsic	3.5
Sedimentary rocks	
Limestone	2.5
Sandstone	0.45
Shale	4.1
Black shale	2 – 300
Phosphorite	50 – 200
Soil	1.0
Plant ash	0.6
Fresh water	0.05 – 1.0 ppb
Sea water	3 ppb

Table 2: Uranium and P<sub>2</sub>O<sub>5</sub> concentrations in some phosphorite deposits

Deposit	U (ppm)	P <sub>2</sub> O <sub>5</sub> (%)	
Turaif (Saudi Arabia)	17	22.3	Al-Bassam (1974)
Al-Sharquia (Syria)	230	22.0	
	60	34.54	
	34	21.40	
Zefa Efe (Palestine)	162	33.59	
Hor Hehar (Palestine)	136	26.59	
El-Quseir (Egypt)	68	23.35	Khalid and Abed, (1981) and Jallad <i>et al.</i> , (1984)
El-Shidiya (Jordan)	67	29.92	
El-Hassa (Jordan)	93	31.12	
El-Russaifa (Jordan)	155	23.3	Al-Lababidi and Banani (1985)
Morroco	120	31	
Hirapur – Basia (India)	130	16.57	Banerjee <i>et al.</i> (1982)
	174	22.23	
Phosphoria Formation (U.S.A.)	90	30.50	Gulbrandsen (1966)

## RADIOACTIVITY OF THE IRAQI PHOSPHORITES

The first discovery of Iraqi phosphorites was achieved by a car-born radiometric survey along Baghdad – Amman highway in the early fifties (Cobbett, 1954). An outstanding radiometric anomaly was recorded about 50 Km west of Rutba, which corresponded to the H<sub>3</sub> phosphorite deposit of Late Cretaceous and Paleocene age. This discovery led later to the discovery of the well known Akashat phosphorite deposit.

The air-born radiometric survey (C.G.G., 1974) showed a remarkable group of semi-continuous anomalies, coded as R7, aligned in a N – S direction at the 40° longitude, from Akashat to Saudi Arabia borders and have extension at the northern rim of Ga'ara depression (Fig.1). The distribution and location of this anomaly group coincide with exposures of Paleocene and Late Cretaceous phosphorite-bearing rock units (Akashat and Digma formations, respectively) (Fig.2).

Gamma logging of phosphorite exploratory boreholes shows intense gamm-peaks coinciding with phosphorite beds and horizons (Fig.3). The intensity of the radiation is proportional to lithology, where the highest peaks are related to friable phosphate-rich horizons. Lower intensity is found where calcite cement is present and the lowest radiation is due to carbonates of low phosphate content.

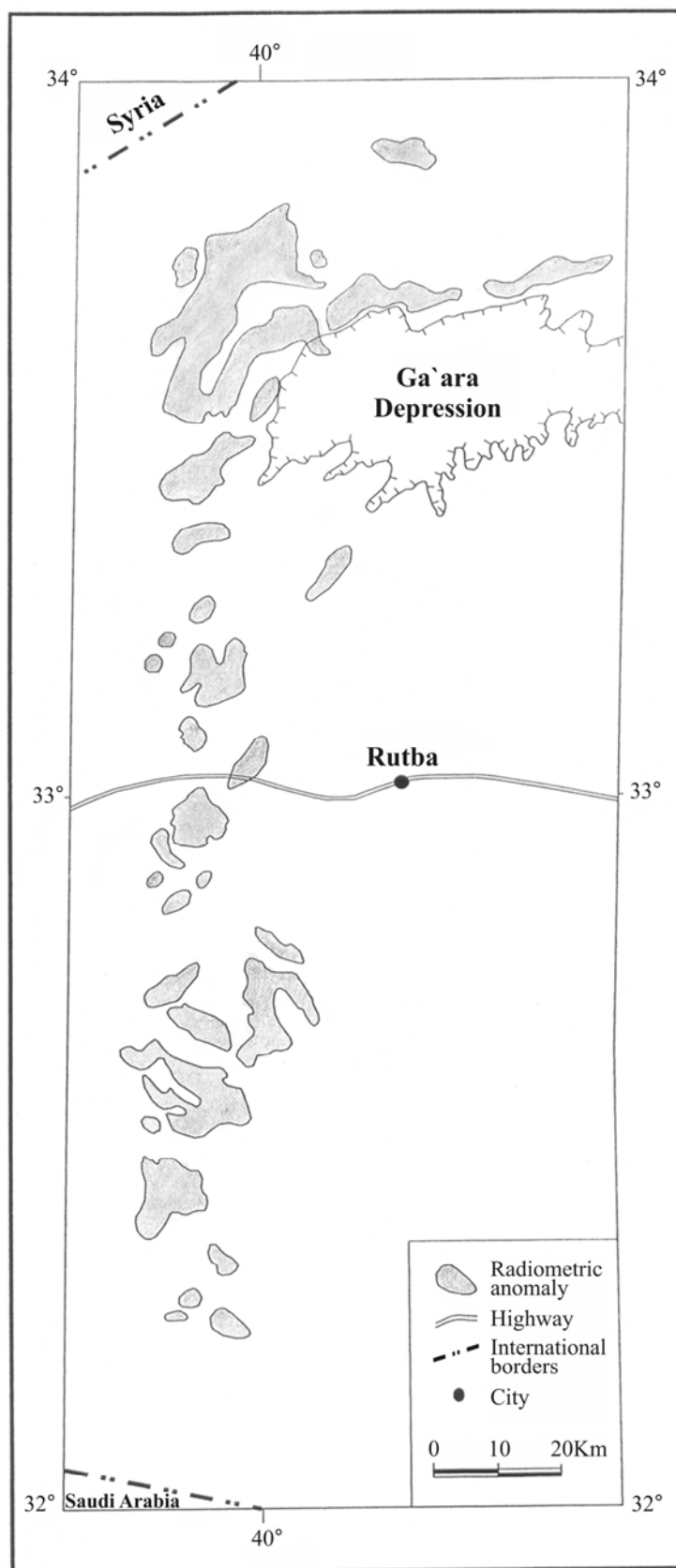


Fig. 1: Distribution of the radiometric anomaly group (R7) in the Rutba area (C.G.G., 1974)

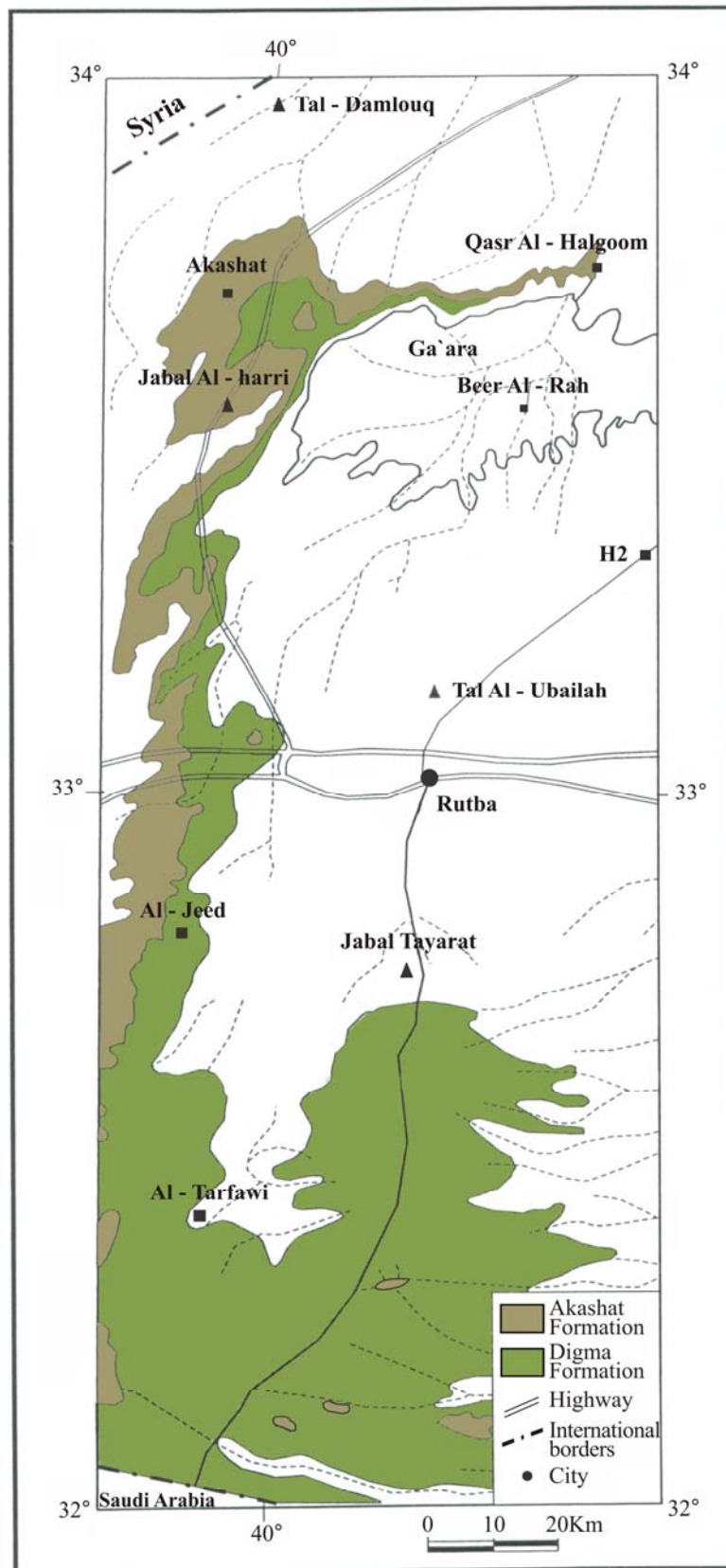


Fig. 2: Spatial distribution of the phosphorite-bearing rock units (Digma and Akashat Formations) in the Rutba area (Sissakian, 2000)

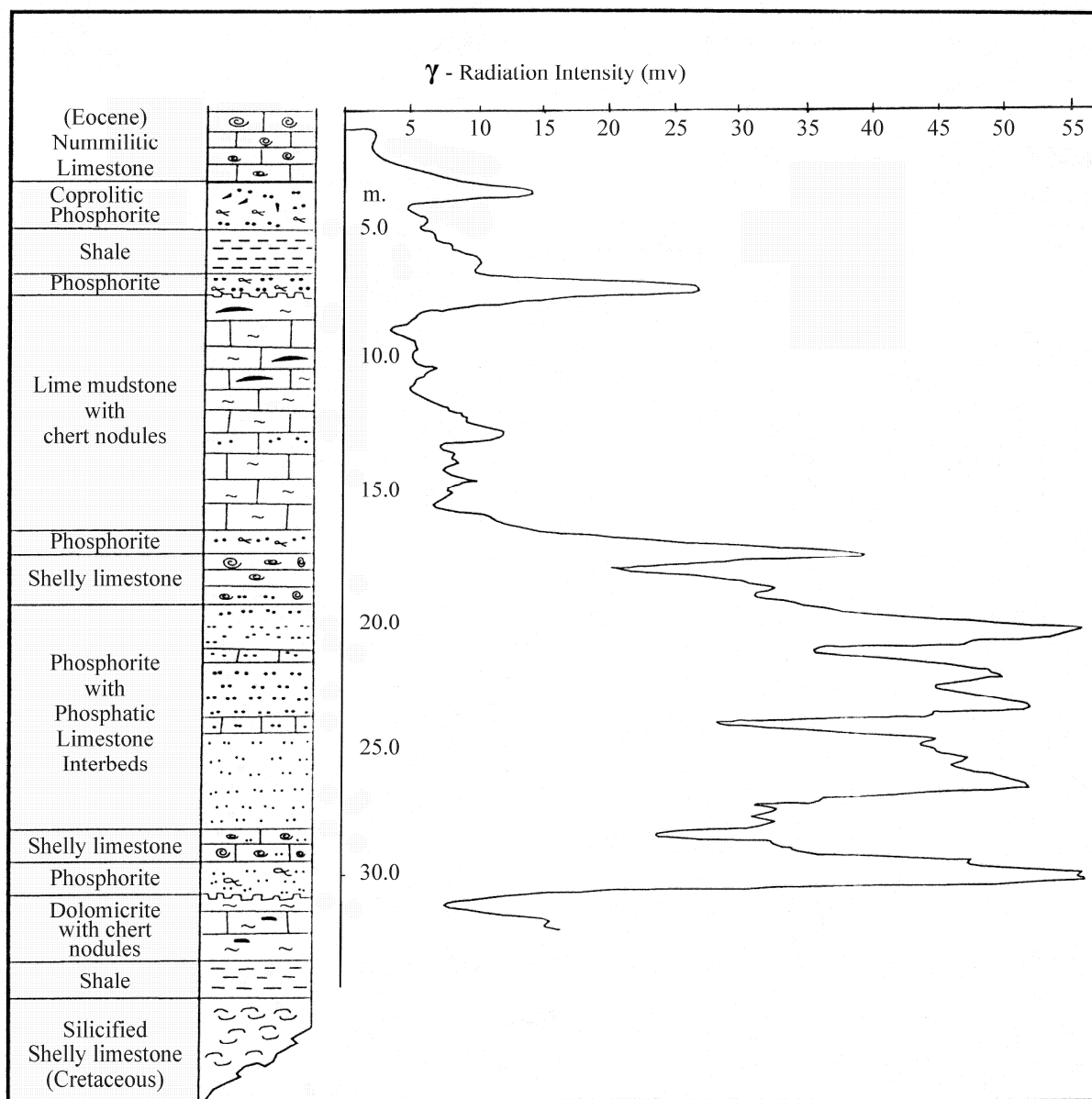


Fig. 3: Gamma-log of the phosphorite-bearing sequence (Paleocene) in Swab Deposit (Al-Bassam, 1988 a)

### URANIUM CONCENTRATION IN IRAQI PHOSPHORITES

The Iraqi phosphorites are found in the following rock units, developed in the Western Desert west of longitude 40° 30'.

**Tayarat Formation** (Late Campanian – Early Maastrichtian )

**Digma Formation** (Late Maastrichtian)

**Akashat Formation** (Paleocene)

**Ratga Formation** (Eocene)

Uranium was analysed in several thousand samples collected from the main phosphorite-bearing rock units in Iraq. All the analyses were carried out by X-ray fluorescence spectrometry (Table 3). The Iraqi phosphorites are relatively poor in uranium; rarely

exceeding 50 ppm, generally ranging from (20 – 45) ppm, corresponding to  $P_2O_5$  content ranging from (12 – 23) %. A general positive relation exists between uranium and  $P_2O_5$ , but the U/  $P_2O_5$  ratio varies within a wide range from about 1.1 to 2.9.

The Paleogene phosphorites show gradual increase in U/  $P_2O_5$  ratio from older (1.52) to younger (2.90) in the investigated phosphorite deposits. The Eocene phosphorites are characterized by the highest U/  $P_2O_5$  ratio (> 2.0), the Paleocene phosphorites show lower values (1.5 – 2.0) and the Late Cretaceous phosphorites show much wider range of U/  $P_2O_5$  values (1.0 – 2.7). Diagenesis and epigenetic modifications may result in enrichment or depletion of uranium in phosphorites depending on the physico-chemical conditions of the environment. Moreover, weathering may result in the leaching and mobilization of uranium. Consequently, many changes in the U/  $P_2O_5$  ratio may occur relative to the original values. In addition, the Late Cretaceous phosphorites are associated with sand and other terrigenous clastics, which may add other sources of uranium not related to phosphate and this may explain the wide range of U/  $P_2O_5$  ratio in these phosphorites.

Table 3: Uranium and  $P_2O_5$  contents of Iraqi phosphorites

### I. Regional Surveys (Al-Bassam et al., 1990)

Formation	Member	U (ppm)	$P_2O_5$ (%)	U/ $P_2O_5$	No. of samples
Tayarat	-----	20	18.53	1.08	6
Digma	-----	39	18.57	2.10	13
Akashat	Traifawi	37	21.09	1.75	27
Akashat	Hirri	34	22.94	1.48	370
Akashat	Dwaima	36	19.69	1.84	103
Ratga	Damluk	37	18.08	2.05	77

### II. Selected deposits

Ref.	Formation	Member/ Unit	Location	U (ppm)	$P_2O_5$ (%)	U/ $P_2O_5$	No. of samples
1	Tayarat	-----	Wadi Sawb	35	12.88	2.72	4
1	Digma	-----	Wadi Sawb	20	11.44	1.75	13
2	Akashat	Traifawi	Marbat	32	21.00	1.52	1044
3	Akashat	Hirri	Sawb	37	21.17	1.70	3600
4	Akashat	Hirri	Akashat	42	21.52	1.95	320
5	Akashat	Dwaima	Area-1	45	21.94	2.05	1110
6	Ratga	Damluk (A)	Nhaidain	45	20.84	2.16	16
7	Ratga	Damluk (B)	Wadi Akash	35	12.05	2.90	13

References: 1) Al-Bassam *et al.* (1983); 2) Gulli (1988); 3) Al-Bassam (1988 a); 4) Al-Bassam (1988 b); 5) Al-Bassam and Saeed (1989); 6) Al-Bassam and Hagopian (1983) and 7) Al-Bassam and Al-Hashimi (1982).

# URANIUM-FRANCOLITE ASSOCIATION

Francolite is the only phosphate mineral in the Iraqi deposits as well as in most marine sedimentary phosphorites of the world. It has a general formula of  $\text{Ca}_{10}(\text{PO}_4\text{CO}_3\text{F})_6\text{F}_2$  where coupled substitution occur for  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  by  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ , respectively. In addition, minor amounts of  $\text{Sr}^{2+}$  and other divalent cations of close ionic radii may substitute for  $\text{Ca}^{2+}$  and anionic groups such as  $\text{VO}_4^{3-}$  may substitute for  $\text{PO}_4^{3-}$ . Francolite is a carbonate fluorapatite where  $\text{CO}_3\text{F}^{3-}$  substitutes for  $\text{PO}_4^{3-}$  and water, as  $\text{H}_3\text{O}^+$ , may be present in substitution for  $\text{Ca}^{2+}$  (McLellan and Lehr, 1969 and McConnell, 1973). More than one technique have been used to show the relation between francolite and uranium in Iraqi phosphorites.

Jemil and Al-Ani (1977) studied alpha particles fission track imprints of a phosphorite sample and found that the radioactivity is limited to the phosphate particles only; non was noticed in the calcareous matrix and cementing material. They concluded that uranium is the source of radioactivity and it is concentrated in the phosphate grains. Ooids and phosphoclasts contained more uranium than bones. Uranium content in various phosphate grains ranges from (70 – 150) ppm, being highest in coprolites, followed by coated grains, peloids and the least in bones. (Aba Husain, 1987).

Al-Bassam and Al-Bedaiwi (1988) correlated gamma intensity with chemically analysed uranium concentration in phosphate-bearing rocks. They found positive correlation between the two, but with significant scattering of points around the best fit correlation line (Fig. 4). Moreover, the correlation is not linear. Both observations were explained by equilibrium state between uranium and its daughter products (e U). Not all the gamma radiation is due to uranium; radium and radon may have significant contribution in this respect. Moreover, gamma radiation may be emitted also by secondary uranium minerals present in these rocks. The authors correlated gamma intensity with  $\text{P}_2\text{O}_5$  and F concentrations (Figs. 5 and 6). The correlation is strongly positive and linear with minor scattering. Phosphorus and fluorine are present only in francolite, where most of the gamma radiation is coming from. Al-Bassam (1977) used X-ray diffraction to relate francolite main peak (211) with  $\text{P}_2\text{O}_5$ , F and U concentrations of phosphorites and phosphatic rocks. The correlation is linear and strongly positive (Figs. 7, 8 and 9) giving no doubt that most of uranium is present in francolite.

Chemical analysis of purified francolite from various Iraqi phosphorite deposits showed increase in uranium concentration, which corresponds to the increase in  $\text{P}_2\text{O}_5$  content (Table 4). The U/  $\text{P}_2\text{O}_5$  ratio in these francolites is within the range found in the enclosing phosphorites (1.2 – 2.9). Values of up to 100 ppm U were found in the Paleocene peloidal – ooidal phosphorites of Akashat.

Table 4: Uranium and  $\text{P}_2\text{O}_5$  concentrations in purified francolites

Formation: Member	U (ppm)	$\text{P}_2\text{O}_5$ (%)	U/ $\text{P}_2\text{O}_5$	Reference
Digma	44	35.48	1.24	Al-Bassam <i>et al.</i> (1983)
Akashat: Hirri	100	33.87	2.95	Al-Bassam (1976)
Ratga: Damluk (A)	60	33.45	1.79	Al-Bassam and Hagopian (1983)
Damluk (B)	92	32.80	2.80	Al-Bassam and Al-Hashimi (1982)



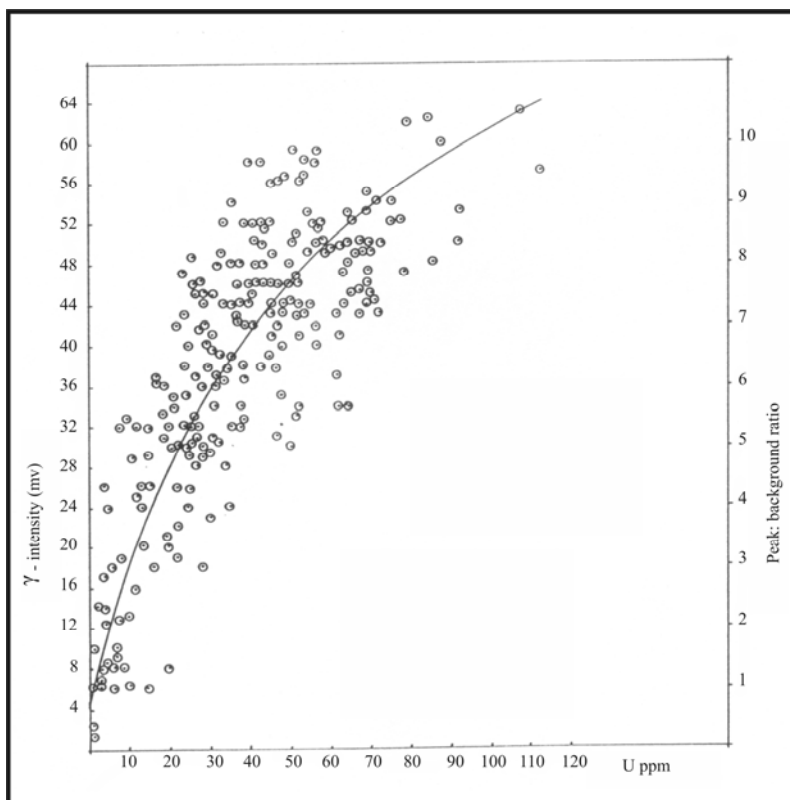


Fig. 4: Relation of gamma intensity and uranium concentration (Al-Bassam and Al-Bedaiwi, 1988)

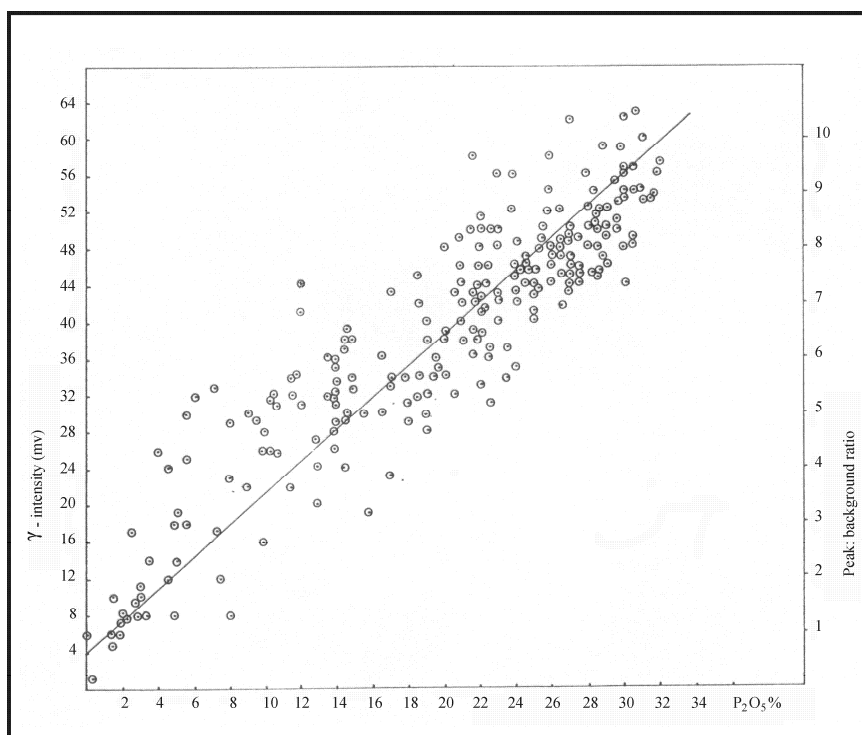


Fig. 5: Relation of gamma intensity and phosphorus concentration (Al-Bassam and Al-Bedaiwi, 1988)

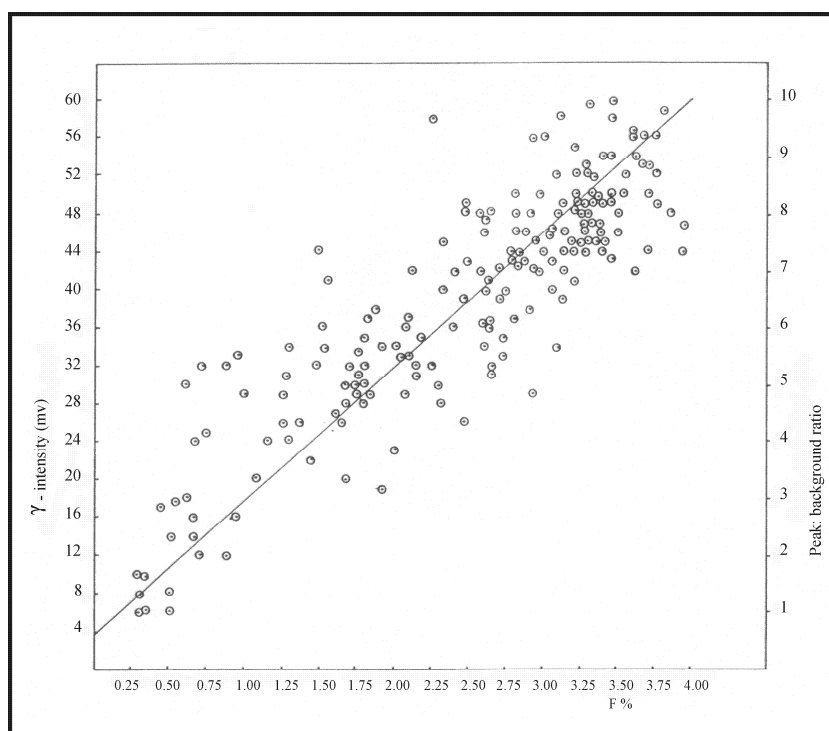


Fig. 6: Relation of gamma intensity and fluorine concentration (Al-Bassam and Al-Bedaiwi, 1988)

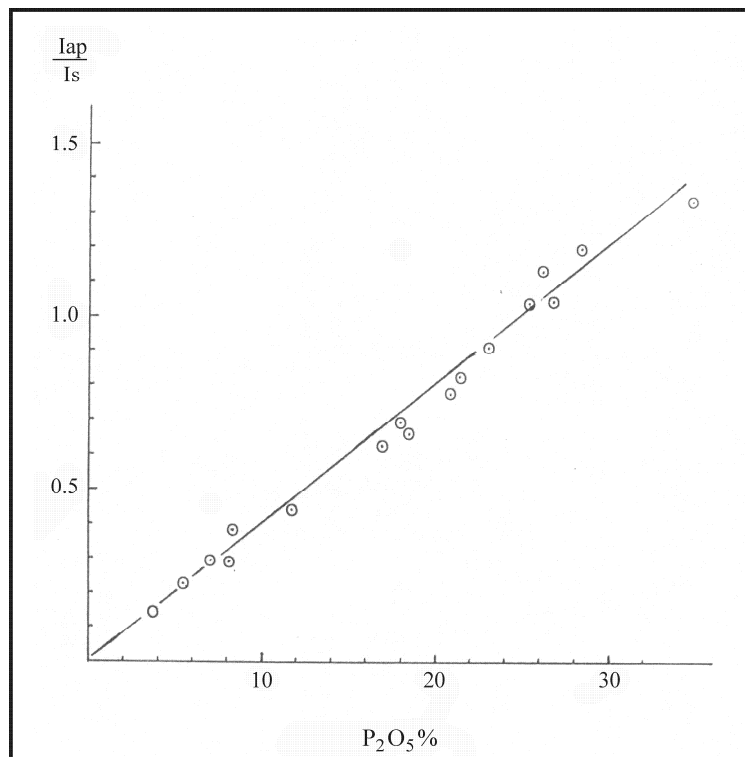


Fig. 7: Correlation between francolite peak and  $P_2O_5$  content (Al-Bassam, 1977)

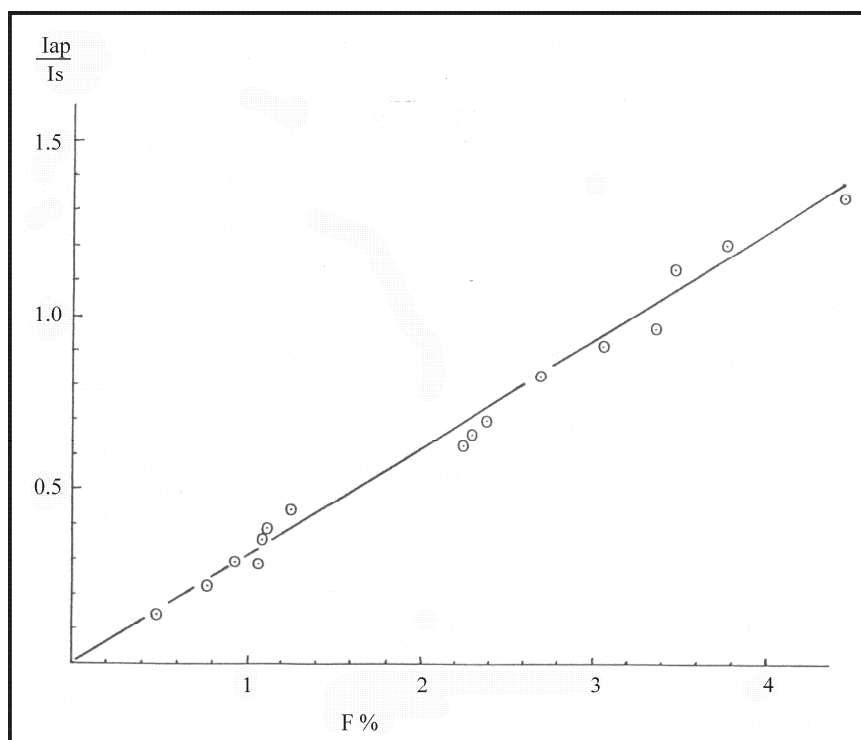


Fig. 8: Correlation between francolite peak and fluorine content (Al-Bassam, 1977)

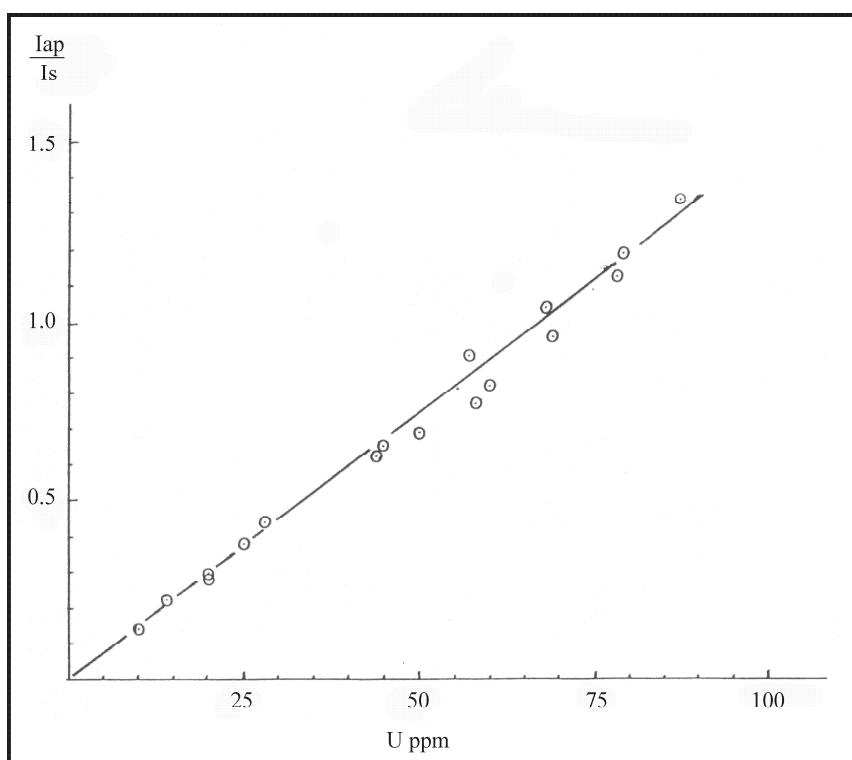


Fig. 9: Correlation between francolite peak and uranium content (Al-Bassam, 1977)

## CRYSTAL CHEMISTRY OF URANIUM IN FRANCOLITE

About 70 years ago McConnell (1938) stated: "The structure of apatite seems to be remarkably stable permitting a number of rather unusual types of substitution and involving a considerable number of ions". This statement proved to be very true in the following years. The apatite structure is remarkably tolerant for a wide range of substitutions in various positions. Strontium, Ba, Pb, Cd, REE and Sn can have complete substitution for  $\text{Ca}^{2+}$  and partial substitution of Ca by Zn, Cu, Co, Ni, and Mg have been demonstrated (Kreidler and Hummel, 1970). Vanadium ( $\text{V}^{5+}$ ),  $\text{S}^{6+}$ ,  $\text{As}^{5+}$ , may substitute for  $\text{P}^{5+}$  in the apatite structure as  $\text{SO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{VO}_4^{3-}$  for  $\text{PO}_4^{3-}$  (Al-Bassam 1975). Fluorine may be replaced by  $\text{OH}^-$  and  $\text{Cl}^-$ .

According to McConnell (1953) and Altschuler *et al.* (1958) uranium, as  $\text{U}^{4+}$ , may enter the apatite structure as a replacement of  $\text{Ca}^{2+}$  in view of the similarity of their ionic radii. Ames (1960) confirmed, by synthesis experiments, that U is not absorbed but enters the structure of carbonate apatite. McConnell (1973) believes that U occurs in both tetravalent and hexavalent states in phosphorites. The tetravalent uranium ( $\text{U}^{4+}$ ) substitutes for  $\text{Ca}^{2+}$  and the hexavalent uranium (as  $\text{UO}_4^{2-}$ ) substitutes for ( $\text{PO}_4^{3-}$ ). It is believed that tetravalent form of uranium predominates at first; at the moment when the original crystallization of apatite occurs, whereas the hexavalent form emerges later, as a result of oxidation. Slansky (1986) however, suggests that the two forms have existed from the beginning.

In view of the very small amounts of uranium in the apatite structure (about 0.0005 atom/ unit cell) it is not expected to show any impact on the cell parameters or optical properties of the mineral. Al-Bassam (1974 and 1976) considered that most of the uranium detected in the Iraqi and East Mediterranean phosphorites is present in the francolite structure as  $\text{U}^{4+}$  replacement for  $\text{Ca}^{2+}$ . Hexavalent uranium can not exist in the highly reducing conditions under which these phosphorites were deposited. Moreover,  $\text{U}^{6+}$  is not stable; it is assumed more loosely bound in the apatite structure (Kolodny and Kaplan, 1970), and can not remain in the apatite structure under oxidizing weathering conditions in view of its high mobility.

## SECONDARY URANIUM MINERALS IN THE IRAQI PHOSPHORITES

Metatyuyamunite ( $\text{CaO} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ ) and carnotite ( $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ ) were identified as secondary uranium minerals in the Iraqi phosphorites (Al-Bassam *et al.*, 1990). They appear as bright yellow stains coating fracture surfaces and filling vugs and pores in these rocks. They tend to occur more in the sequence overlying main phosphorites beds in exposed sections. Very little of these minerals have been noticed in subsurface sections. Metatyuyamunite is common in phosphorites and limestone, whereas carnotite is more common in shale.

The mobility of uranium is highly dependent on its oxidation state, Eh and pH of the environment. Hexavalent uranium is extremely mobile under alkaline and oxidizing conditions (Dall'aglio *et al.*, 1974).

Obviously most of uranium was originally present in the francolite as  $\text{U}^{4+}$  in view of the reducing conditions of phosphorite deposition (Al-Bassam, 1976). Some of the tetravalent uranium was later oxidized under atmospheric weathering to  $\text{U}^{6+}$  and eventually left the francolite structure as uranyl anionic group. Part of this uranium may have been lost into circulating water, but the remaining part was fixed by the formation of very insoluble vanadate complexes of Ca and / or K.

Vanadium may have been supplied mostly from francolite, where  $\text{VO}_4^{3-}$  can substitute for  $\text{PO}_4^{3-}$  to a limited extent (McConnell, 1973). The oxidation of carbonaceous matter associated with phosphorite may have been another source. The Iraqi phosphorites contain (70 – 180) ppm vanadium (Al-Bassam *et al.*, 1990). Seasonal fluctuation of the water-table,

under semi-arid climate may have facilitated the precipitation of these secondary minerals (Al-Fadhli and Abdul Qadir, 1969).

Kolodny and Kaplan (1970) presented an interesting theory relating radioactive decay with the oxidation of  $U^{4+}$ . According to their idea, uranium is present as two main isotopes in francolite:  $U^{234}$  and  $U^{238}$ . There is a preferential oxidation of  $U^{234}$  as compared to  $U^{238}$ . Hence there is an "escape" of  $U^{238}$  from  $U^{4+}$  to  $U^{6+}$ . During radioactive transformation from  $U^{238}$  to  $U^{234}$ , oxidation of  $U^{4+}$  to  $U^{6+}$  may occur due to several factors according to Kolodny and Kaplan (1970):

- Formation of positively charged ions during Alpha decay.
- Stripping of two electrons as a result of the recoil.
- Increase in the positive charge of the ions due to Beta decay.

### EQUILIBRIUM STATE OF URANIUM IN IRAQI PHOSPHORITES

Radiometric analysis of  $U_3O_8$  and equivalent e  $U_3O_8$  show scattering around the 1:1 equilibrium line (Fig.10). The  $U_3O_8$  content in 25 determinations ranges from (11 – 89) ppm (mean 56 ppm) and the e  $U_3O_8$  content varied from (38 – 79) ppm (mean 59 ppm).

Uranium in the analysed phosphorites is almost in a state of equilibrium with its daughter (Ra). A slight shift may be noticed in favor of Ra in the diagenetically affected phosphorites where porosity is high due to leaching of the cementing material.

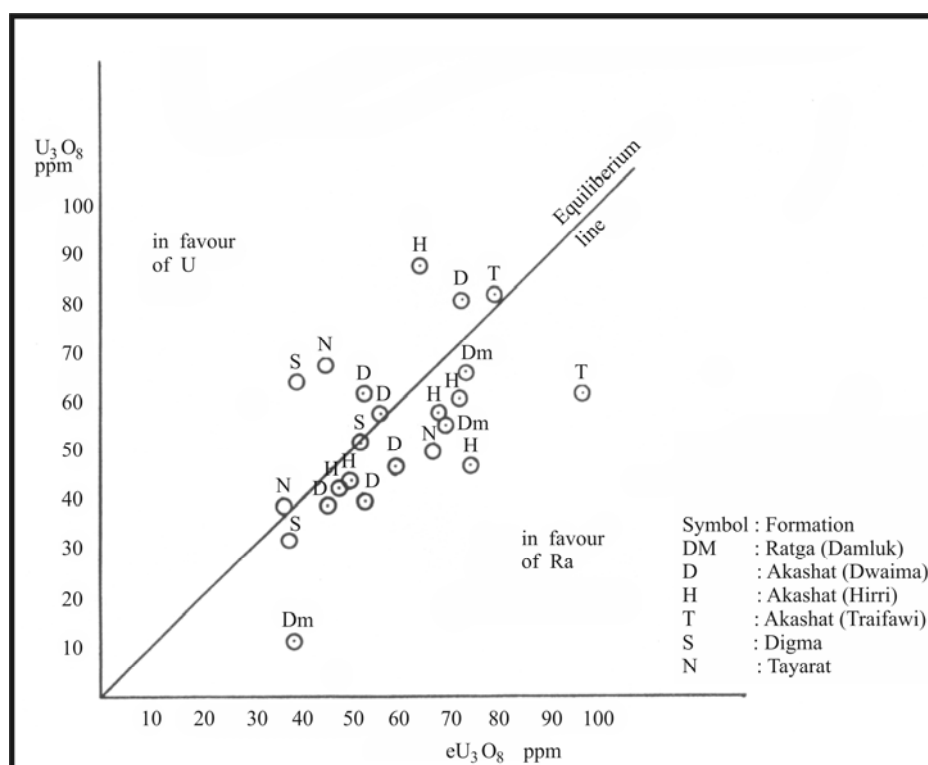


Fig. 10: Uranium equilibrium state in some Iraqi phosphorites (Al-Bassam *et al.*, 1990)

## SOURCE OF URANIUM IN THE MARINE PHOSPHOGENIC SYSTEM

Rivers provide the main supply of uranium to the marine environment. It is transported in fresh water as the most soluble uranyl carbonate ion  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  (Adler, 1974). The availability of uranium brought by rivers to the phosphogenic system depends on the environment.

Data on recent phosphorites formation show that the immediate source of uranium in phosphorites is not sea water (which contains  $3 \times 10^{-6}$  gm/l U), but the enclosing sediments, which contain up to  $60 \times 10^{-4}$  % U and the interstitial waters, which contain up to  $650 \times 10^{-6}$  gm/l U (Baturin, 1982).

Strong reducing conditions are expected in the interstitial environment (Eh about -200 mv), but it seems that despite these conditions, uranium has a certain degree of mobility and apparently occurs as metallo-organic complexes (Baturin, 1982). It is the great geochemical affinity of uranium to phosphorites (Rankama and Sahama, 1950) and the reducing conditions of phosphogenesis that attract uranium to marine phosphorites. Francolite acts as a collector of uranium in marine environments and considered, together with black shale, as the major uranium sink in these environments.

The terrigenous source of uranium in the Iraqi phosphorites is demonstrated by the work of Aha Husain (1987). Uranium to  $\text{P}_2\text{O}_5$  ratio in phosphorites increases shore-ward from 0.5 to 2.0. Major rivers in the Late Cretaceous and Early Tertiary (?) brought clastics (Marbat Beds) and uranium (?) to the near-shore marine environment. The U/  $\text{P}_2\text{O}_5$  ratio in the phosphorites decreases away from the influence of these rivers (Fig. 11).

During the Late Cretaceous and Paleogene marine transgression covered most of the Western Desert of Iraq, but the core of the Horan High remained exposed including Ga'ara and neighbouring areas (Figs.12 and 13). Uranium-rich sandstones are known in the Ga'ara Formation (Permocarboniferous) (Al-Quwaizi, 1997) and in the Amij Formation (Middle Jurassic) (Ismail, 1996). Both formations were exposed at that time (Al-Bassam *et al.*, 1999). Most of the uranium in the Iraqi phosphorites could have been supplied from such source rocks and transported to the shallow parts of the sea by river as uranyl carbonate ion.

The Iraqi phosphorites are granular in texture and it is believed that most of the phosphate was deposited in the intestinal environment via biological (microbial) phase (Al-Bassam, 1976 and Al-Bassam *et al.*, 2000). The intestinal environment and the reducing conditions of such environment provided excellent opportunity for uranium intake by the phosphate at the early stages of crystallization. However, submarine reworking and sorting by currents and waves may have resulted in further enrichment of the phosphate grains by uranium as suggested by the significant variation in the U/  $\text{P}_2\text{O}_5$  ratio.

## RADIOACTIVITY OF PHOSPHORAITE AS AN EXPLORATION TOOL

The radioactivity of marine sedimentary phosphorites provides an excellent tool of surface and subsurface exploration for phosphorites. Air-born, car-born and even hand-born radiometric surveys can be very useful in locating surface exposures of phosphorites. Gamma logging of drilled wells and boreholes provides further technique for subsurface exploration. Many phosphorite deposits in the East Mediterranean region were discovered in this way including the Iraqi deposit of H<sub>3</sub>.

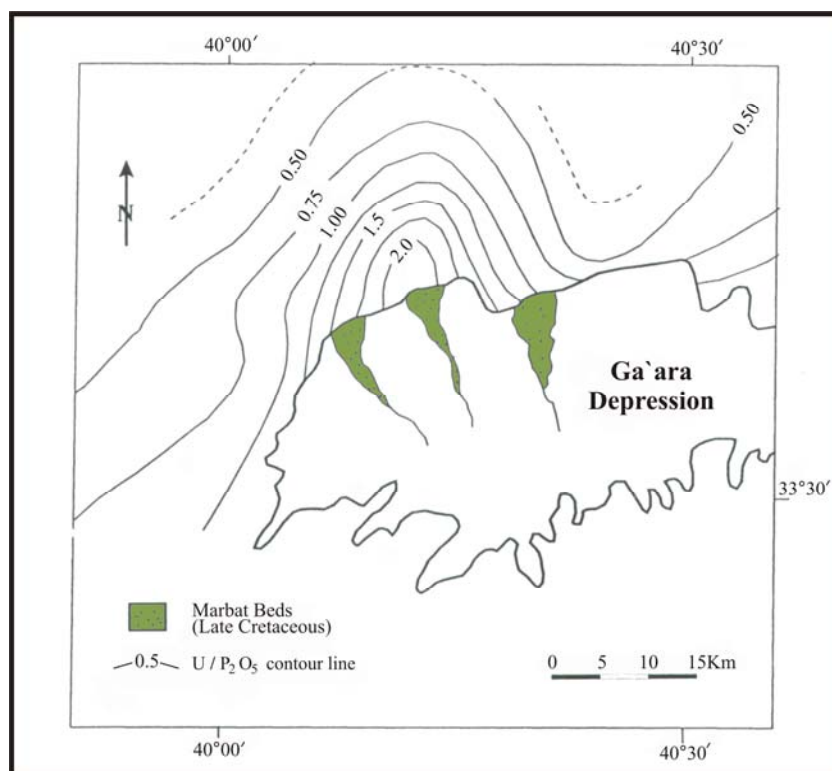


Fig. 11: Distribution of U/ P<sub>2</sub>O<sub>5</sub> ratio in the Paleocene phosphorites, north of Ga'ara Depression (Aba Husain, 1989) and location of Marbat Beds in the area (Al-Bassam *et al.*, 1986)

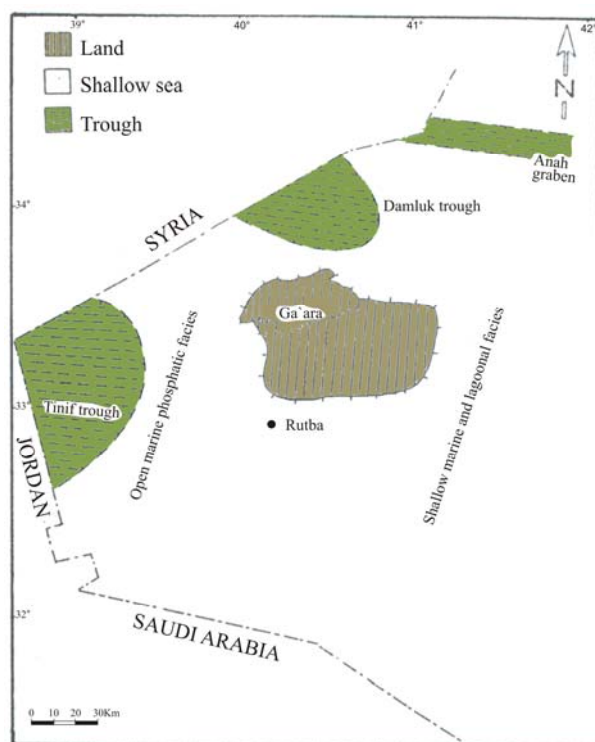


Fig. 12: Paleogeography of the Late Campanian – Maastrichtian in Western Desert (Al-Bassam *et al.*, 1999)

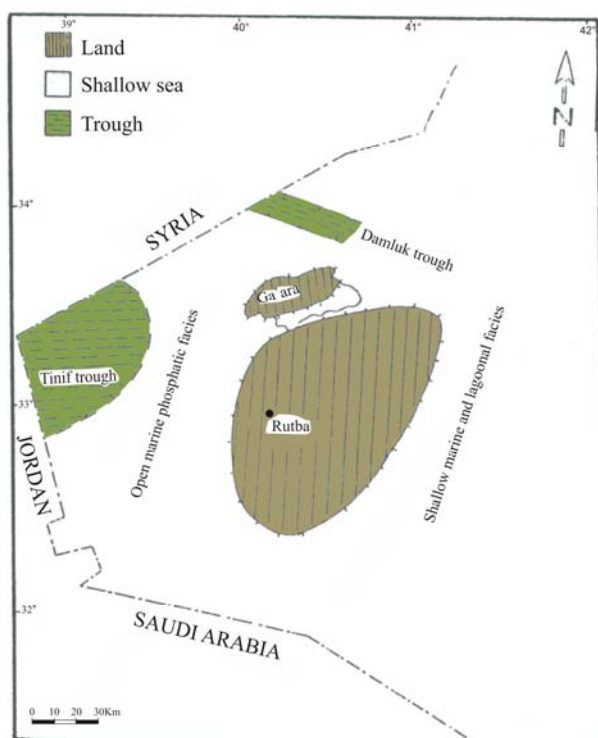


Fig. 13: Paleogeography of the Paleogene in Western Desert  
(Al-Bassam *et al.*, 1999)

To Gamma logging of phosphorite exploration boreholes was used to control drilling accuracy and thickness measurements (Al-Bedaiwi, 1990 in: Al-Bassam *et al.*, 1990). An attempt was made to use gamma logging results in grade evaluation of  $P_2O_5$  and U concentrations. The technique was successful for a rapid estimation of phosphorite grade in the field (Al-Bassam and Al-Bedaiwi, 1988). The match between gamma intensity and the concentration of  $P_2O_5$  and U was very satisfactory (Fig. 14).

#### ENVIRONMENTAL IMPACT OF U-BEARING PHOSPHATE FERTILIZERS

The process of fertilizers production from phosphate rocks in Iraq requires calcinations of the crude phosphate and desliming to remove the  $CaCO_3$  cement and to obtain a phosphate concentrate of about (30 – 32) %  $P_2O_5$ . In this process, uranium is concentrated together with  $P_2O_5$  to about (60 – 65) ppm U (Al-Qaragulli, 1983). However, in the next stage of phosphoric acid production, uranium is fractionated between phosphoric acid and phosphogypsum (by-product). It is estimated that about 75% of the original uranium remains in the phosphoric acid, and consequently in the final fertilizer products. It is estimated that the phosphate fertilizers produced in Iraq after 1991 contains about 40 ppm U.



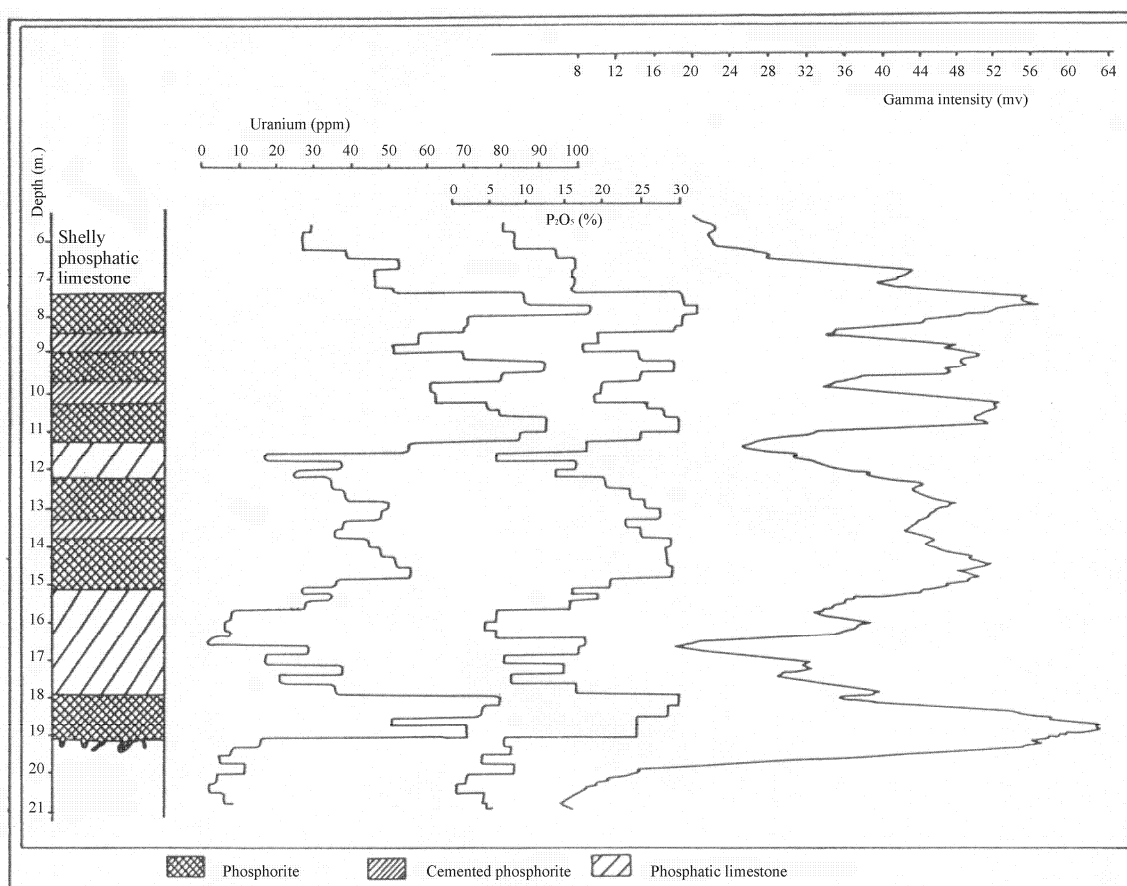


Fig. 14: Gamma intensity,  $P_2O_5$  and U concentration in BH. D3 – Quarry 5, Akashat (Al-Bassm *et al.*, 1990)

In view of the alkaline nature of Iraqi soils (Sillanpaa, 1982) uranium will be in ionic state (as uranyl carbonate) following the dissolution of the phosphate fertilizer within the soil water. There is no barrier for this uranium to be taken by plants and finally entering the food cycle. Moreover, the excess U-bearing irrigation water may be transferred to shallow groundwater aquifers causing serious contamination. There is no data to support these pessimistic points of view, but in the mean time there is no scientific objection to deny them. Most phosphate fertilizer-producing countries strip their products from uranium at the phosphoric acid stage as an environmental protection measure. Uranium is a hazardous element and its concentration should be monitored in soil, water and air in order to control its intake by humans and animals.

## CONCLUSIONS

- The radioactivity of the Iraqi phosphorites is mainly due to uranium incorporated in the francolite structure (as  $U^{4+}$ ) and to a lesser extent to secondary uranium minerals and decay products of uranium.
- Uranium in the studied phosphorites appears to be nearly in equilibrium with its decay products (e U).

- Metatyuyamunite and carnotite are the only secondary uranium minerals detected in the Iraqi phosphorites. The former is associated with phosphorite and limestone and the latter with shale.
- The source of uranium is terrigenous, brought by rivers from uranium-rich clastics to the depositional site and was incorporated in the francolite structure due to the strong geochemical affinity of U to phosphates and was stabilized from mobilization by the strong reducing conditions of the environment. Post depositional enrichment or depletion of uranium from the phosphorites could have taken place for many reasons of epigenetic and weathering modifications.
- The radioactivity of phosphorites is a very efficient tool of prospecting and exploration in surface and subsurface surveys.
- The presence of significant concentrations of uranium in the phosphate fertilizers produced in Iraq may cause very serious hazard to the environment.

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