

Secondary uranium in phosphorites and its relation to groundwater in Egypt

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The stratiform phosphorite deposits of Egypt, which are found in an east-west band between 24° and 27° north latitude, contain from 25 to 100 ppm uranium, a significant portion of which can be shown to have been secondarily adsorbed from groundwater. This fraction is readily leachable in 0.2 N K₂CO₃ and in the Red Sea area has the same ²³⁴U/²³⁸U activity ratio, 1.3, as the U dissolved in the associated groundwater. Both the excess of ²³⁴U and the deficiency of ²³⁰Th relative to ²³⁸U shows that the leachable U was adsorbed within the last 250 ky. Secondary U with the same ²³⁴U/²³⁸U activity ratio also occurs in the Western Desert phosphorite, indicating that it too has been adsorbed relatively recently, even though the groundwater table today is well below the phosphatic strata. On the other hand, the leachable U in the intervening Nile Valley deposits has an activity ratio near 1.0, suggesting that those strata have been above the groundwater table for the last million years. The adsorption of U may not be entirely associated with the principal phosphate mineral, carbonate-fluorapatite (francolite), Ca₅(PO₄,CO₃)(F,OH). Iron, organic and clay phases are also present in the phosphorite ore.

INTRODUCTION

Stratified phosphorite ore is important as an economic deposit in Egypt, with uranium as a potential economic by-product of phosphate production. There are three major mining areas: the Western Desert between the Kharga and Dakhla Oases, the Nile Valley near Idfu, and along the Red Sea between Safaga and Quesir (Fig. 1). These deposits yield ore containing 90% phosphate and from 25 to 100 ppm uranium. Of lesser importance are phosphate deposits in the Sinai Peninsula, which are of lower grade and considered to be commercially insignificant. The total phosphate reserves in Egypt are estimated to exceed 3 billion tons (Notholt, 1985), and although their contained U would exceed 100,000 tons, recovery of U from Egyptian phosphorites is conducted only on an experimental basis by the Nuclear Materials Authority of the Egyptian government (Ali, 1990).

A recent review by Sharafeldin (1999) has summarized the uranium occurrences as well as the clay mineralogy of the Egyptian deposits. Dabous (1981), El Kammar and El Reedy (1984), Ahmed (1986), Tamish (1988), Mahdy (1989), and Ali (1990) have focused on the geochemistry of uranium in Egyptian phosphorites, while Kolodny (1981), Osmond *et al.* (1984), and Burnett and Veeh (1992) have reviewed the U-series disequilibria often exhibited by phosphorites. In recently deposited phosphorites 40 to 80 percent of the contained U is in the +4 valence state, signifying mostly reducing conditions of deposition (Cathcart, 1978; Kolodny and Kaplan, 1970; Burnett and Veeh, 1992).

The radionuclides investigated during this study are part of the two natural decay series, of which ²³⁸U and ²³²Th are the parents (Fig. 2). The U content and uranium isotope activity ratio of ²³⁴U/²³⁸U (*AR*) has been found to be especially useful in the interpretation of the history of aqui-

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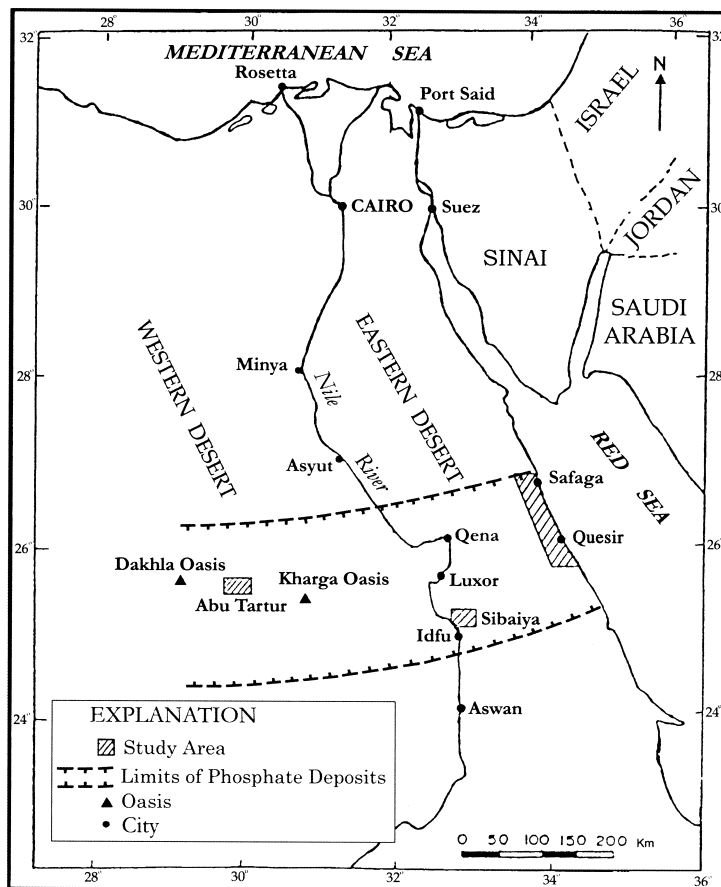


Fig. 1. Map of Egypt showing the location of the three studied mining areas; from West to East: Western Desert, Nile Valley, Red Sea.

fer waters and their leaching effects on the aquifer rocks (Osmond and Cowart, 2000).

It is the purpose of this study to examine the evidence for the presence of secondary uranium in the Egyptian phosphorites and to determine to what extent the timing of its adsorption from groundwater can be established.

BACKGROUND

Geology and mineralogy

The phosphorite ore deposits of Egypt are part of the Mediterranean Phosphate Province, which extends from Morocco to Turkey, and consists of strata deposited on the shallow Tethyan sea floor during Late Cretaceous and Early Tertiary time.

Over a band of Egypt between 24° and 27°N latitude these strata are nearly horizontal but in the Red Sea area folding and block faulting have resulted in tilting of the mineable beds. The phosphate beds are estimated to contain in excess of 3 billion tons of ore (Notholt, 1985). Most of these reserves are in the Abu Tartur area.

In the region of the Eastern Desert (Red Sea Coast) the phosphorite-bearing strata are known as the Duwi Formation (Youssef, 1957), in the Nile Valley region as the Sibaiya Phosphate Formation (Youssef, 1957; El Nagger, 1966) and in the Western Desert as the Phosphate Formation (Awad and Ghobrial, 1966). These beds rest with seeming conformity on the Nubia sandstones and are overlain by the deeper water marls and chinks of

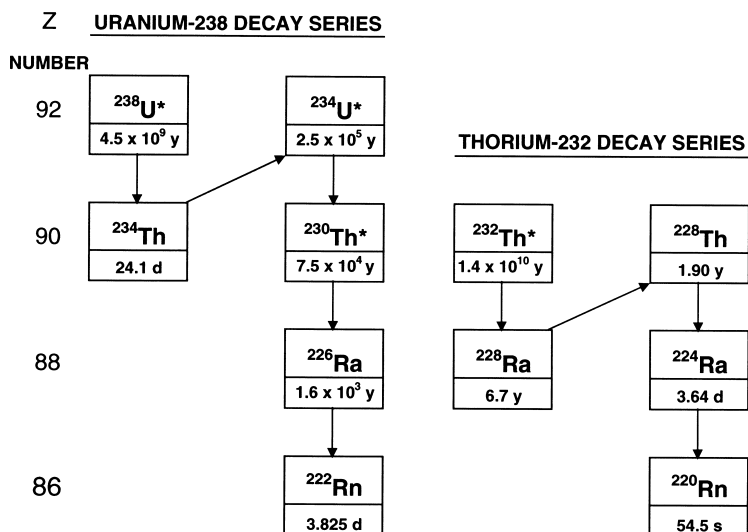


Fig. 2. The radioactive decay series of ^{238}U and ^{232}Th . The asterisks indicate the four long-lived naturally occurring nuclides measured in this study. The uranium isotopes ^{238}U and ^{234}U were measured in all the groundwater and phosphorite samples. The thorium isotopes ^{232}Th and ^{230}Th were measured in the Red Sea phosphorites.

the Dakhla formation (Fig. 3).

The mineralogy of the Egyptian phosphorite deposits has been studied by many investigators (El Baz, 1970; Abu-Zeid, 1974; El Kammar, 1974; Kamel *et al.*, 1977; Dabous, 1981; Sharafeldin, 1999). The major phosphorite mineral is carbonate-fluorapatite (francolite). The non-phosphatic minerals are represented by dolomite, calcite, quartz, pyrite, goethite, gypsum, smectite, and kaolinite. In the Western Desert palygorskite is recorded by Sharafeldin (1999) and wavellite is recorded by Kamel *et al.* (1977) and Shaaban and Dabous (1987).

The clay minerals associated with Egyptian phosphorites occur mainly as a matrix or as a filling of the intergranular pores. Some clay minerals are also present as parts of the phosphatic pellets, or as fillings of the cavity-like microstructures in the bone and teeth fragments. Smectite is the dominant clay mineral, followed by kaolinite, whereas illite and palygorskite are present in trace concentrations (Sharafeldin, 1999). Palygorskite occurs in the form of mats made up of ribbon-like fibers commonly associated with flaky smectite crystals that coat dolomite rhombohedra

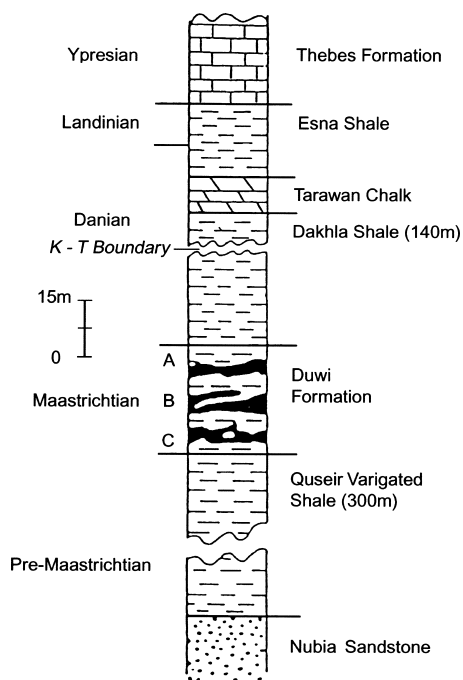


Fig. 3. General stratigraphic column of the Quesir-Safaga district, showing the location of the phosphorite deposits. A, B, and C are the major phosphorite seams of the Duwi Formation in the Quesir-Safaga area (after Said, 1990a).

(Sharafeldin, 1999). This mode of occurrence has also been reported in the Miocene phosphorites of Florida (Van Kauwenbergh *et al.*, 1990; Compton, 1997), the Cretaceous phosphorites of Morocco (Prevot, 1990), and the Jordanian Cretaceous phosphorites (Khoury *et al.*, 1988).

The iron minerals goethite, hematite, and pyrite have been found as coatings on the outer surfaces of phosphate pellets and as parts of the cementing material (Dabous, 1981, Sharafeldin, 1999).

HYDROGEOLOGY

The general relationship of the Nubia Aquifer to the phosphate beds has been outlined by Dabous (1994). The depth to the water table of the Nubia Aquifer is more than 200 m at Kharga Oasis and more than 1000 m in the Nile Valley (Shata, 1982).

The hydrogeology of the Safaga-Quesir area in the Eastern Desert is described by Gomaa (1992), El Ghazawi and Abdelbaki (1991), and El Fakharani (1989). The mountainous area in the Eastern Desert is bisected by two sets of drainage lines, which conduct their water either to the Red Sea or to the Nile Valley. The Red Sea drainage set is included in the present study. This drains the Safaga-Quesir area, which includes the major basins of Safaga, Queh-Saqia, Ambagi-Abu Ziran and Essel, from north to south. The groundwater is tapped from different water-bearing formations, including alluvial deposits (Quaternary), sandstone deposits (Miocene-Oligocene), limestone deposits (Cretaceous), sandy gypsum-bearing shale-marl sediments (Cretaceous), and basement rocks.

The hydraulic gradient of groundwater in the limestone aquifer in the Duwi Formation decreases from north to south, from +39.94 m to +28.92 m above sea level. The water level in the same aquifer decreases in the southeast direction from +46.26 m in the Queh mining area to +22 m in the Abu Shigili mining area (Gomaa, 1992). The groundwater movement in the limestone aquifer is affected by the fault system that is located on the floor of the aquifer sediments. The dominant

trend of this fault system is NNW-SSE parallel to the Red Sea graben (Issawi *et al.*, 1969).

Uranium geochemistry

Uranium has two naturally occurring valence states. In shallow oxic-carbonate aquifers it has a +6 valence and is quite soluble as soluble carbonate complexes. In deep reducing aquifers it has a +4 valence and is generally insoluble. Host rocks containing phosphatic, argillaceous, or organic material often behave as ion exchange media for otherwise soluble uranium. The most abundant isotope, ^{238}U , is the decay chain parent of daughter ^{234}U , and in closed systems older than 10^6 years the two are in radioactive equilibrium, i.e., the $^{234}\text{U}/^{238}\text{U}$ alpha activity ratio is unity ($AR = 1.00$). However, because of enhanced mobilization of the daughter isotope by decay-related alpha recoil effects most ground waters have dissolved U with AR 's greater than 1.00, while many mineral surfaces and adsorption coatings have U with AR 's less than 1.00. Therefore mobilization of U often involves isotopic fractionation. On the other hand, precipitation or adsorption causes no fractionation and the secondary U will have the same AR as the ground water source.

Once previously mobile U is incorporated into the solid phase, the excess ^{234}U ($AR > 1.00$) decays toward equilibrium according to its 250 ky half-life.

METHODS

Field collections

Thirty-five ore samples were collected from the three principal phosphate mining areas in Egypt (Fig. 1): 12 samples from Abu Tartur (Western Desert), 12 from Sibaiya (Nile Valley), and 11 from Safaga-Quesir district (Red Sea coast).

The samples for this study were taken from the lower 4 m thick phosphate horizon in the Abu Tartur mining district of the Western Desert. In the Sibaiya mining district of the Nile Valley samples were also taken from the lower of two commercial beds. In the Safaga-Quesir (Red Sea) region, Said (1990a) has subdivided the Duwi For-

mation into three phosphate horizons (A, B, and C of Fig. 3), each of which was sampled. The ore beds are tilted as a result of block faulting, and are lenticular rather than uniform in thickness (Hussein, 1990).

In addition twelve water samples were collected from the surficial aquifer of the Red Sea region, where the ore is largely below the water table. The water samples were collected in 4 liter plastic bottles, acidified with 20 ml concentrated nitric acid, and filtered through a 0.45 microns pore-size filter.

Mineralogy and chemical analyses

The mineralogy of the phosphorite ore was determined by X-ray diffraction analyses (XRD), carried out at the Florida State University MARTECH laboratory, using a Siemens Diffractometer connected to DIFFRAC-AT software.

Total concentrations of Ca, P, Fe, and V in 27 samples from the three mining areas were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The analyses were performed at the Activation Laboratories, Ontario, Canada. A 0.25-gram aliquot of sample is digested in 10 ml fuming $\text{HClO}_4\text{-HNO}_3\text{-HCl-HF}$ at 200°C and is then diluted to 10 ml with dilute aqua regia. The solutions are read on a simultaneous Jarrell Ash ICP spectrometer. The precision of these analyses is $\pm 5\%$, all of the components being present at more than 100 times detection limits.

Uranium and uranium isotopic analyses

The ore samples were ground to pass a 230 mesh ($<63\ \mu\text{m}$) screen. Two grams were dissolved with 8N hydrochloric acid, and the weights of the insoluble residue were determined. Another 2 grams were subjected to 0.2N K_2CO_3 leaches at $\text{pH} = 12$ for 24 hours at 70°C (Weinberg and Cowart 2001). Previous leaching studies showed that apatite dissolution is not an important process (Roe and Burnett, 1985). The resulting analyzed phases of the phosphorites were designated as soluble (S), leachable (L), and soluble-

unleachable (F).

A known quantity of ^{236}U spike and a carrier consisting of ferric nitrate were added to each of the S and L samples. The samples were boiled and ammonia solution added for precipitation of ferric hydroxide. The resulting $\text{Fe}(\text{OH})_3$ floc is separated from supernatant liquid by centrifugation. The iron was separated from the actinides by solvent extraction with diethyl ether. The U was further purified by anion exchange procedures (Bio Rad AG 1×8 , 100–200 mesh). Both hydrochloric and nitric acid stages of anion exchange were used. The resulting purified and separated uranium was electroplated onto stainless steel planchets for counting by alpha spectrometry. Details of the procedures are given by Lally (1992). The uncertainty of both the U concentration values and the U isotopic ratios was a uniform $\pm 5\%$, inasmuch as a fixed-count protocol was used.

Repeated calibrations were performed using an NBS marine phosphate standard (SRM-120C). Our result was uranium content of 115.0 ± 4.6 ppm, essentially identical to the reported value of 114.5 ppm with a $^{234}\text{U}/^{238}\text{U}$ activity ratio of 0.92 ± 0.03 .

After the water samples were evaporated, the dissolved uranium was determined by alpha spectrometry in the same way as the ore samples.

Thorium isotopic analyses

The soluble phases of the Red Sea suite of phosphate samples were also analyzed for their thorium isotopic composition using ^{229}Th as a yield tracer. ^{232}Th is the more abundant common thorium isotope and ^{230}Th the radiogenic daughter of ^{234}U (Fig. 2). Because Th is insoluble under all natural ground water conditions, there should be very little original ^{232}Th in the phosphorite and any ^{230}Th should be the result of ingrowth following deposition. The dating equation derives from:

$$(1 - ^{230}\text{Th}/^{234}\text{U}) = \exp(-\lambda t) \quad (1)$$

where λ is the decay constant of ^{230}Th (75 ky), and t is the time since deposition of the U.

Table 1. Chemical data of the Egyptian phosphorites

Sample number*	P ₂ O ₅ %	CaO %	Fe ₂ O ₃ %	V ppm	U _T ppm	U _L	CaO/P ₂ O ₅	U _T /P ₂ O ₅
W-01A	37.11	44.67	5.12	67	25.9	2.6	1.20	0.70
W-02A	21.21	42.02	4.54	42	16.2	1.3	1.98	0.76
W-03A	32.01	44.99	4.61	64	23.5	2.5	1.41	0.73
W-04A	19.21	42.24	5.78	42	17	2.0	2.20	0.88
W-05B	29.03	44.33	6.01	56	22.8	2.8	1.53	0.79
W-06B	21.77	43.05	6.78	54	24	2.8	1.98	1.10
W-07B	23.02	43.01	4.76	48	21.5	1.9	1.87	0.93
W-08B	26.11	43.92	2.99	59	23.4	0.8	1.68	0.90
W-09B	33.98	44.21	5.01	59	22.6	2.3	1.30	0.67
W - MEDIAN	26.11	43.92	5.01	56	22.8	2.00	1.68	0.79
N-01C	27.33	49.34	2.21	66	53.9	0.0	1.81	1.97
N-02C	27.32	49.11	2.31	74	53.5	0.2	1.80	1.96
N-03C	28.85	48.44	2.37	73	59.8	0.3	1.68	2.07
N-04C	26.42	47.33	3.99	75	53.3	24.5	1.79	2.02
N-05C	21.21	41.81	1.41	49	42.3	0.0	1.97	1.99
N-06C	29.99	49.89	2.77	77	64.7	1.9	1.66	2.16
N-07C	25.99	44.55	2.31	71	45.9	0.0	1.71	1.77
N-08C	31.01	48.85	2.17	69	63.5	0.7	1.58	2.05
N-09C	31.66	49.32	2.44	74	63.2	0.1	1.56	2.00
N-10C	30.34	48.89	2.01	75	64.2	0.1	1.61	2.12
N-11C	25.12	42.01	1.71	58	52.9	1.4	1.67	2.11
N - MEDIAN	27.33	48.85	2.31	73	53.9	0.2	1.67	2.02
R-01D	31.02	47.78	2.01	143	119.8	1.7	1.54	3.86
R-02D	26.11	50.99	1.65	93	100.2	1.5	1.95	3.84
R-03E	21.21	45.91	1.84	87	60.2	1.1	2.16	2.84
R-04E	30.77	52.01	0.63	131	120.1	0.3	1.69	3.90
R-05E	24.89	45.01	1.11	112	93.3	1.1	1.81	3.75
R-06G	24.88	47.83	2.31	101	109.8	2.1	1.92	4.41
R-07G	22.51	46.78	1.99	107	112.2	1.6	2.08	4.98
R - MEDIAN	24.89	47.78	1.84	107	109.8	1.00	1.92	3.86

U_T = Total uranium concentration in the whole sample, U_L = Leachable uranium, * = Sample locations are shown in Table 2. Note: Modal precision values are +/-5%.

Phase data analysis

The total uranium, in micrograms per gram of original phosphorite, was determined for the S (soluble) and the L (leachable) fractions, and that of the F fraction by difference:

$$U_F = U_S - U_L \quad (2)$$

(The U_T values in Table 1 tend to be somewhat lower than the U_S values in Table 2, because the former percentages are based on the whole ore samples, including the insoluble components.)

The $^{234}\text{U}/^{238}\text{U}$ activity ratio was also measured directly on the S and L fractions and that of the F fraction by differences, using the formula of Osmond and Cowart (1982):

$$A_F = A_S - (U_L/U_F) (A_L - A_S) \quad (3)$$

where U_F and U_L are the total U in the F and L phases; A_S , A_L , and A_F are the activity ratios in the soluble, leachable, and non-leachable phases respectively.

Table 2. Uranium concentration and activity ratio in phosphate phases

Sample number	Per cent insoluble residue	U in phosphate (ug/g)			U activity ratio ($^{234}\text{U}/^{238}\text{U}$)		
		S	L	F	S	L	F
W-01A	6.5	27.7	2.6	25	1.03	1.08	1.02
W-02A	5.5	17.1	1.3	16	0.92	1.65	0.86
W-03A	9.0	25.8	2.5	23	0.94	1.73	0.84
W-04A	5.0	17.9	2.0	16	0.89	1.26	0.84
W-05B	14.7	26.7	2.8	24	1.01	1.25	0.98
W-06B	5.0	25.3	2.8	23	1.01	1.25	0.98
W-07B	6.0	22.9	1.9	21	1.03	1.40	1.00
W-08B	9.3	25.8	0.8	25	1.00	1.39	0.99
W-09B	6.7	24.2	2.3	22	1.01	1.25	0.98
W-10B	9.7	4.1	0.3	4	1.10	1.62	1.06
W-11B	2.7	45.9	7.5	38	1.12	1.09	1.13
W-12B	7.7	22.9	0.0	24	0.96	2.10	0.96
W-MEDIAN	6.6	25.0	2.0	23	1.01	1.35	0.98
N-01C	6.5	57.6	0.0	58	1.05	1.00	1.05
N-02C	5.7	56.7	0.2	57	1.01	2.00	1.01
N-03C	9.4	66.0	0.3	66	1.03	0.98	1.03
N-04C	5.6	56.4	24.5	32	1.04	1.04	1.04
N-05C	0.4	42.5	0.0	44	1.00	1.34	1.00
N-06C	9.1	71.1	1.9	69	1.14	1.01	1.14
N-07C	37.4	73.4	0.0	75	1.18	1.07	1.18
N-08C	9.3	70.0	0.7	69	1.03	1.03	1.03
N-09C	9.8	70.1	0.1	70	1.01	1.08	1.01
N-10C	2.8	66.0	0.1	66	1.01	1.11	1.01
N-11C	26.9	72.3	1.4	71	1.07	0.89	1.07
N-MEDIAN	9.4	66.0	0.2	65.9	1.03	1.04	1.03
R-01D	4.4	125.2	1.7	124	0.99	1.99	0.98
R-02D	2.4	102.7	1.5	101	1.14	1.25	1.14
R-03E	0.9	60.7	1.1	60	1.09	1.15	1.09
R-04E	3.6	124.6	0.3	124	0.98	1.56	0.98
R-05E	3.9	97.1	1.1	96	1.02	1.46	1.01
R-06G	2.2	112.2	2.1	110	1.01	1.23	1.01
R-07G	1.2	113.6	1.6	112	1.04	1.26	1.04
R-08H	2.4	54.7	0.0	55	1.02	1.20	1.02
R-09 I	15.8	58.8	0.0	59	1.03	1.32	1.03
R-10J	4.4	86.9	1.9	85	0.99	1.27	0.98
R-11J	2.5	94.6	1.9	93	1.01	1.32	1.00
R-12J	0.5	106.7	2.7	104	1.04	1.38	1.03
R-MEDIAN	2.4	100.0	1.0	99.0	1.02	1.30	1.02

KEY: W = Western Desert, N = Nile Valley, R = Red Sea, S = soluble, L = leachable, F = unleached, A = Abu Tartur Old Mine, B = Abu Tartur New Mine, C = Sibaiya Mine, D = Um El Huwitat Mine, E = South Rabah Mine, G = Mohamed Rabah Mine, H = Quesir Old Mine, I = Abu Shigli Mine, J = Queh 3H Mine.

Note: Modal precision values are +/-5%.

RESULTS

Mineralogy of the phosphorites

Carbonate-fluorapatite (francolite) is the major phosphate mineral in the Egyptian deposits as

reported by Dabous (1981). Contaminants present include such non-phosphatic Ca-bearing minerals as calcite, dolomite, and gypsum.

The presence of these contaminants is also indicated by the chemical analyses summarized in

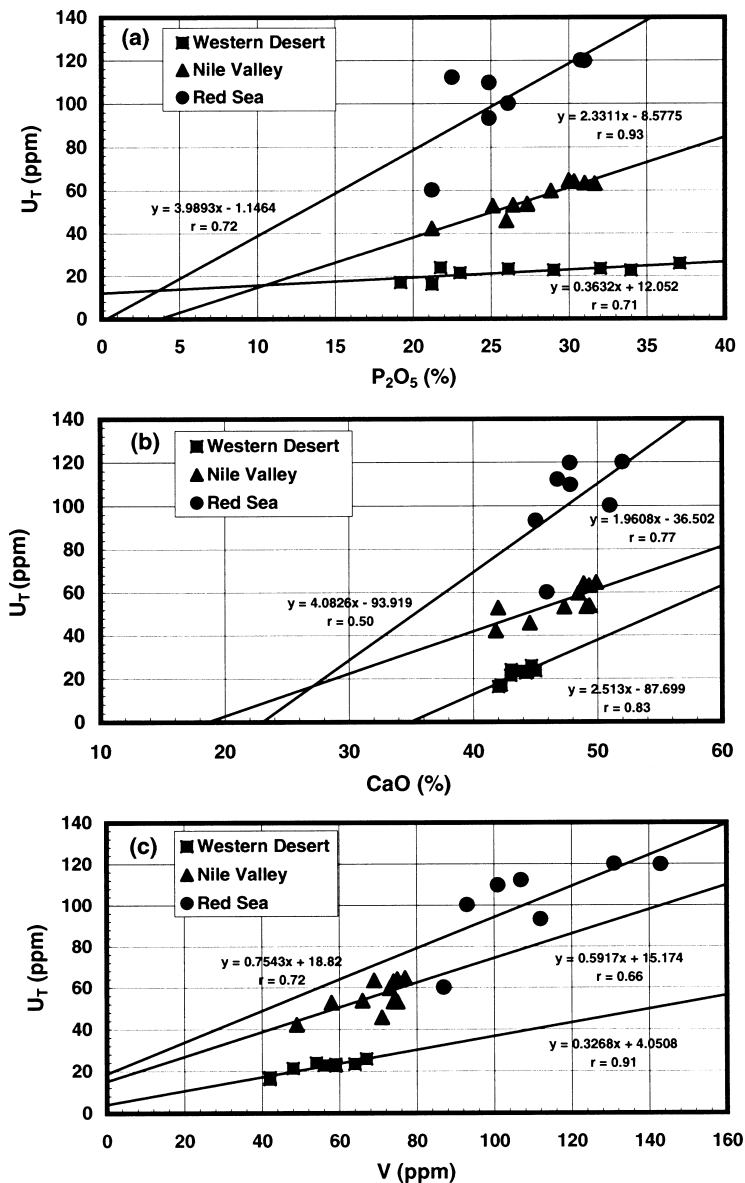


Fig. 4. Covariants of U in Egyptian Phosphorites: (a) U and P_2O_5 . The linear covariations shown by all three sample suites show that the U is associated with the phosphate minerals, with highest concentrations in the Red Sea area, and least in the Western Desert. (b) U and CaO. The linear covariations show that the U is associated with some Ca-bearing mineral such as francolite. That there is a significant non-zero intercept on the x-axis shows that there are other Ca minerals present which are not U-bearing, such as calcite, dolomite, and gypsum. The relative tenor of U in the three areas is the same as in (a) above: Red Sea > Nile Valley > Western Desert. (c) U and V. The linear covariation lines show that V and U are associated together in the phosphate minerals. The significant y-axis intercepts is indicative of secondary U in the ore.

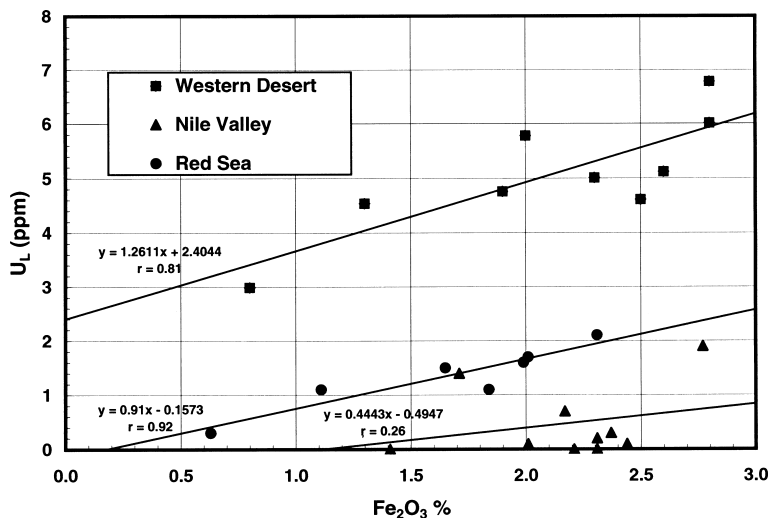


Fig. 5. The covariation of leachable uranium to iron content is especially strong in the Western Desert and the Red Sea samples, which suggests that the oxides of iron are adsorbing U from groundwater. The Western Desert phosphorites, which have the least amount of total U (Fig. 4), have the largest amount of leachable U.

Table 1. The ideal CaO to P₂O₅ ratio for pure apatite would be 1.32 and could be as high as 1.55 in francolite depending on the amount of carbonate substituting for the phosphate radical (Dabous, 1981). The values for this ratio in the Egyptian phosphorites (1.67 to 1.92) is somewhat larger than expected and would be accounted for by the presence of calcite, dolomite, and gypsum. The highest ratio is observed in the Red Sea ores, where the X-ray diffractograms showed that the chief contaminant is calcite.

Uranium in the phosphorites

The concentration of uranium in the Egyptian phosphorites increases eastward, 25 ppm in the Western Desert, 66 ppm in the Nile Valley deposits, and 100 ppm in the Red Sea deposits (Table 2, Figs. 1 and 4). This is believed to be related in some way to the paleogeography of the Tethyan Seaway, but might also be coincidental.

That U is associated with the francolite is shown by its correlation with both P₂O₅ (Fig. 4a) and CaO (Fig. 4b). The non-zero intercept of the graph of U with CaO means that there is little association of U with the non-phosphate minerals, calcite, dolomite and gypsum. The association of

vanadium with U (Fig. 4c) suggests that both elements are incorporated into the francolite lattice in similar fashion. On the other hand, iron, though often associated with V and U, shows poor correlation with these two elements in the Egyptian phosphorites, suggesting the possibility that Fe, like U, is introduced later.

A broad peak on the X-ray diffractograms of the Red Sea samples indicates the presence of non-crystalline material, probably organics, which confirms the findings of El Kammar (1974) and Dabous (1981). This suggests the possibility that some of the uranium is adsorbed on organic material in the samples.

U in the leachable and unleachable phosphate phases

Leaching of the phosphate ores with K₂CO₃ removes a measurable amount of U: 8% of the total U in the Western Desert samples, about 1% of that in the Red Sea samples, and 0.3% of the U in the Nile Valley samples (Table 2). The uranium present in the Western Desert appears to be less concentrated but unusually soluble compared to that of the other two districts. In both the Western Desert and the Red Sea phosphorites there is a

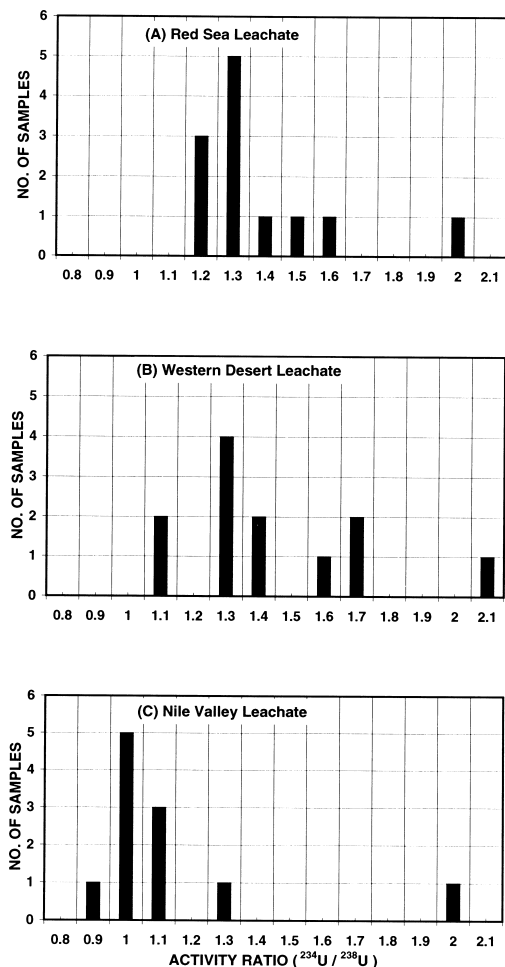


Fig. 6. Histograms of $^{234}\text{U}/^{238}\text{U}$ activity ratio of leachate samples from the three study areas. The modal value for leachable U activity ratio in the Western Desert and Red Sea areas is about 1.3. For the Nile Valley samples this value is close to 1.0 (equilibrium).

strong correlation between leachable uranium (U_L) and Fe_2O_3 (Fig. 5). This suggests that oxides of iron could be acting as sorbants for uranium from groundwater. This leachable U has a $^{234}\text{U}/^{238}\text{U}$ activity ratio of about 1.3 which is distinctly higher than the unleached U ratio of about 1.0 (equilibrium) in the case of the Western Desert and Red Sea phosphates. In the Nile Valley samples both the leachable and non-leachable U has the activity ratio of equilibrium (Fig. 6).

These results contrast with leaching experi-

ments on marine phosphate nodules which show no preferential extraction of U (Altschuler *et al.*, 1958; Gavshin *et al.*, 1973).

Thorium in the soluble phosphate phase

After removal of the resistate phases of the Red Sea samples, the soluble phosphate samples were analyzed for their thorium as well as uranium isotopic content (Table 3). As expected, the $^{232}\text{Th}/^{238}\text{U}$ concentration ratio was quite low, making possible the measurement of a meaningful dating ratio, i.e., $^{230}\text{Th}/^{234}\text{U}$. Eight samples yielded ages ranging from 84 to 161 ky and one 201 ky, while three proved to be more than 350 ky old.

Uranium in the groundwater of the Red Sea area

Apparently the U in the leachable phases has been adsorbed from groundwater at some time after initial deposition of the phosphate beds. This is proven by the considerable amount of U adsorbed on the grain exteriors in all three areas, and the disequilibria of the adsorbed U in the Red Sea and Western Desert areas. The phosphatic strata are tilted in the Red Sea area (Said, 1990a), so that in some places the ores are in contact with the groundwater below the present day water table. The concentration of U in these groundwater is quite variable, from 0.024 to 22 ppb, but the $^{234}\text{U}/^{238}\text{U}$ activity ratio is consistently high (Table 4).

In Fig. 7 the activity ratio data is plotted against reciprocal U concentration of the dissolved U in the groundwater from the Red Sea area. This is a mixing-type diagram (Osmond and Cowart, 2000) which, if straight-line trends are observed, can be used to infer (a) the excess ^{234}U content of the groundwater and (b) the leaching activity ratio of the dissolved U. In the Red Sea area, three groundwater regimes can be identified, having disparate amounts of dissolved excess ^{234}U , but a similar leaching ratio of 1.3 to 1.6.

That the leaching ratio of the dissolved U in the Red Sea groundwater is identical to the leachable U of the phosphorite constitutes further confirmation that U is being exchanged between ore and water. The abundance of U in the leachable

Table 3. Thorium analyses and $^{230}\text{Th}/^{234}\text{U}$ ages of Red Sea secondary uranium

Sample number	U ppm	Th ppm	Activity ratios			Age ky
			$^{230}\text{Th}/^{232}\text{Th}$	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$	
R-01D	125.2	11.6	21	0.99	0.70	130
R-02D	102.7	4.6	30	1.14	0.66	118
R-04E	124.6	8.6	40	0.98	0.98	>350
R-05E	97.1	1.5	126	1.02	0.66	118
R-06G	112.2	8.2	29	1.01	0.70	130
R-07G	113.6	5.5	34	1.04	0.54	84
R-08H	54.7	4.0	41	1.02	1.01	>350
R-09I	58.8	10	22	1.03	0.71	134
R-10J	86.9	21.7	9	0.99	0.78	161
R-11J	94.6	3.6	66	1.01	0.84	201
R-12J	106.7	2.1	163	1.04	1.03	>350

Note: Modal precision values are $\pm 5\%$.

Table 4. Uranium isotopic data of groundwater in the Safaga-Quesir area of the Red Sea Region

Locality	Sample number	Well designation	Depth (m)	Uranium concentration (ppb)	Reciprocal concentration	Activity ratio ($^{234}\text{U}/^{238}\text{U}$)
Safaga	1-A	Um El Huwitat Mine	150	6.739	0.15	1.58
	2-A	South Rabah Mine	25	0.956	1.05	1.40
	3-A	Mohamed Rabah Mine	17	2.457	0.41	1.25
	4-A	Wasif Mine	—	0.143	6.98	2.83
	5-A	Queh-1	10	0.33	3.03	1.86
Quesir	1-B	Queh 3H Mine	55	0.035	28.35	1.98
	2-B	Abu Shigli Mine	—	0.065	15.43	1.63
	1-C	Queh-2H	156	0.024	42.26	2.18
	2-C	Quesir Old Mine	15	0.304	3.28	1.28
	1-D	Abu Spaq	4.5	21.719	0.05	1.66
	2-D	Abu Korab	4.6	5.284	0.19	1.69
	3-D	Ambagi Spring-1	—	4.755	0.21	1.82

A = Limestone Aquifer (Duwi Formation, Safaga), B = Limestone Aquifer (Duwi Formation, Quesir), C = Sandstone Aquifer (Nubia Sandstone, Quesir), D = Alluvial Aquifer (Alluvial Deposits, Quesir).

Note: Modal precision values are $\pm 5\%$.

outer rinds of phosphate grains shows that the dominant process for the last million years ($T_{1/2}$ of $^{234}\text{U} = 250$ ky) has been adsorption.

DISCUSSION

U adsorption in the phosphorites

The fact that a significant portion of the U, especially in the Red Sea district, is removable

by gentle leaching shows that much of the U in the Egyptian phosphorites is adsorbed rather than contained in the francolite lattice. The presence of iron in the analysis may indicate that, rather than the phosphorite itself, iron oxides may be the sites of adsorption. Borovec (1981) reports on experiments in which dissolved uranyl complexes are readily adsorbed on iron oxyhydroxides, organic matter, and montmorillonite clay.

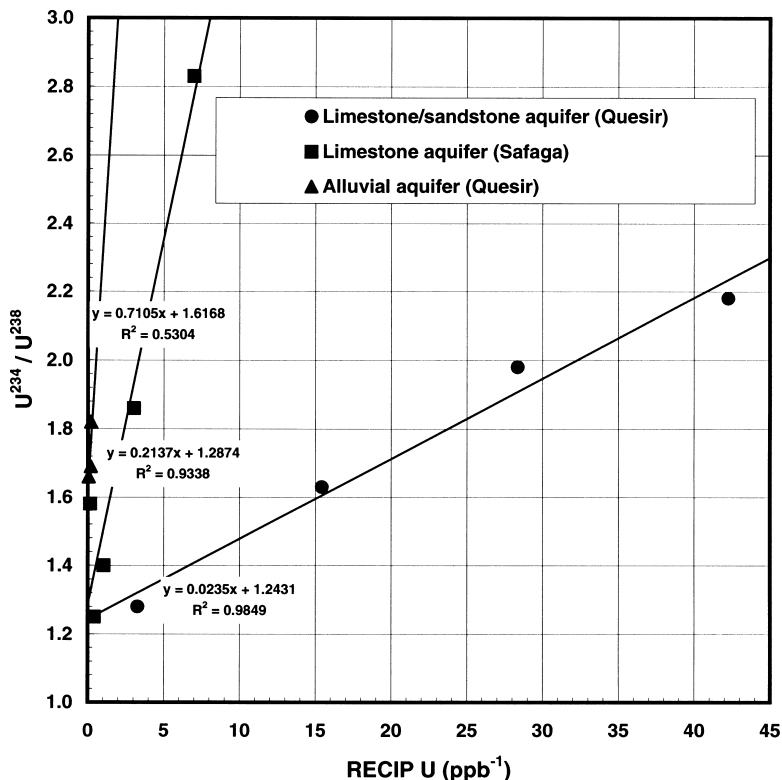


Fig. 7. Uranium isotopic mixing plot of the Safaga-Quesir groundwater. The three regression lines on this plot indicate possible water/rock interactions for three parts of the aquifer as a whole, the limestone aquifer near Safaga, the limestone/sandstone aquifer near Quesir, and the alluvial aquifer at Quesir. For each line the y intercepts show the $^{234}U/^{238}U$ activity leaching ratio and the slopes the dissolved excess ^{234}U in the aquifer waters. Of the three leaching systems the alluvial aquifer at Quesir has the highest concentration of excess ^{234}U , and the nearby deeper limestone/sandstone aquifer the lowest. The two strata-bound aquifers have the same indicated $^{234}U/^{238}U$ leaching ratio at 1.24 to 1.29. The leaching intercept of the uranium in the alluvial aquifer is indicated to be higher, at 1.62, but given the uncertainty range of the intercept of this steeply sloping line it is not clear whether this leaching ratio is significantly different than the other two. All of the three leaching ratios are consistent with the activity ratios of the leachable uranium in the Red Sea phosphates (see A.R. histogram of Fig. 6).

On the other hand even the purest francolite samples analyzed here and elsewhere do contain U, presumably somewhere in the lattice. That such U remains sensitive to the hydrologic environment is shown by the preponderance of +6 U in surficial island phosphorites (Roe and Burnett, 1985), and also in the oxidized groundwater of Florida (Upchurch and Randazzo, 1997; Weinberg and Cowart, 2001).

Climatic History

Changing climatic conditions over the last few

million years in North Africa would have altered groundwater regimes episodically. For example the Sahara Desert was fertile, with abundant lakes, streams, and high groundwater tables only 8 ky ago (Said, 1990b; Dabous and Osmond, 2001). Osmond *et al.* (1999) and Dabous (2002) have identified a pattern of leaching and redeposition associated with pluvial conditions in the U and Fe deposits of the Egyptian Sahara. It is hypothesized here that the same climatic events have caused the changes in water table and the remobilization of U in the phosphorites.

The high *AR* of the U in the Red Sea phosphorites, and also in the Western Desert phosphorites, as measured in this study, are an indication that the mobilization and redeposition of the U occurred relatively recently in terms of the half-life of ^{234}U , 250 ky. The $^{230}\text{Th}/^{234}\text{U}$ ages show that the time of this adsorption was mainly during oxygen isotope climatic stages 5 and 6, 84 to 161 ky (Table 3).

CONCLUSIONS

The U content of the Egyptian phosphorites varies from one mining locality to another with the highest concentration, 100 ppm, being found in the Red Sea deposits, and the lowest, 25 ppm, in the Western Desert deposits. About 8% of the uranium is readily leachable in the Western Desert, but less than 1% in the other two areas. The leachable U has a $^{234}\text{U}/^{238}\text{U}$ activity ratio near 1.3 in the Western Desert and Red Sea deposits, but is close to the equilibrium value of 1.0 in the Nile Valley deposits. The Red Sea deposits occur partly within the local groundwater, which has a variable amount of dissolved U, up to 22 ppb U, with an activity ratio of 1.3. One can conclude from this that in the Red Sea region there is an active exchange of U between the groundwater and the U adsorbed on some phases of the phosphorite. If the same process occurred in the Western Desert deposits, the groundwater table must have been lowered below the horizontal ore beds less than a million years ago. Conversely, the groundwater table in the Nile Valley mining district must have been lowered more than a million years ago.

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