

# Sedimentological, mineralogical and geochemical characteristics of Upper Cretaceous Egyptian phosphorites with special reference to the microbial role in phosphogenesis

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**Abstract:** The Upper Cretaceous phosphorites of Egypt are associated with either siliciclastic or carbonate facies. SEM investigations of freshly fractured phosphorite samples have revealed the presence of various ultrastructures. Non-phosphatized fossil micro-organisms, phosphatized grains with tubular structures, phosphatized diatoms and apatite crystals are the common ultrastructures encountered. The phosphatized diatoms indicate the important role of algae in phosphogenesis. The dissolution of diatoms creates new porosity favourable for apatite growth and releases silica which participates in chert, porcellanite (usually shell porcellanite) and glauconite formation associated with phosphorites.

X-ray diffraction examination of the studied samples has demonstrated that carbonate-fluorapatite (CFA) is the only phosphate mineral encountered. A noticeable variation in the chemistry of the carbonate-fluorapatite is evident from the microprobe results. Carbonate-fluorapatites associated with phosphorite-bearing siliciclastics are relatively enriched in FeO, MgO and Na<sub>2</sub>O, whereas those associated with phosphorite-bearing carbonates are relatively enriched in CaO and F, a result which illustrates the effect of facies control on CFA chemistry.

48 representative phosphorite samples, in particular of the economic phosphorites, were analyzed using XRF techniques for their major oxide and trace element content. The results show that the content of trace elements vary in the phosphorites belonging to similar grade. This may be attributed to facies control and/or the existence of micro-organisms.

**Keywords:** Phosphorite, Phosphogenesis, Egypt, Upper Cretaceous, Algae, Geochemistry

## 1. INTRODUCTION

The economically utilized Upper Cretaceous phosphorites of Egypt were deposited during the transgression of the Tethyan Sea, forming a 100–150km wide belt stretching from the Red Sea in the east into the Western Desert in the west. Due to the considerable economic interest in Egyptian phosphorites, their mineralogy and chemistry have been previously dealt with by many scientists (e.g. El TABLAWI, 1966; GHANEM et al. 1971

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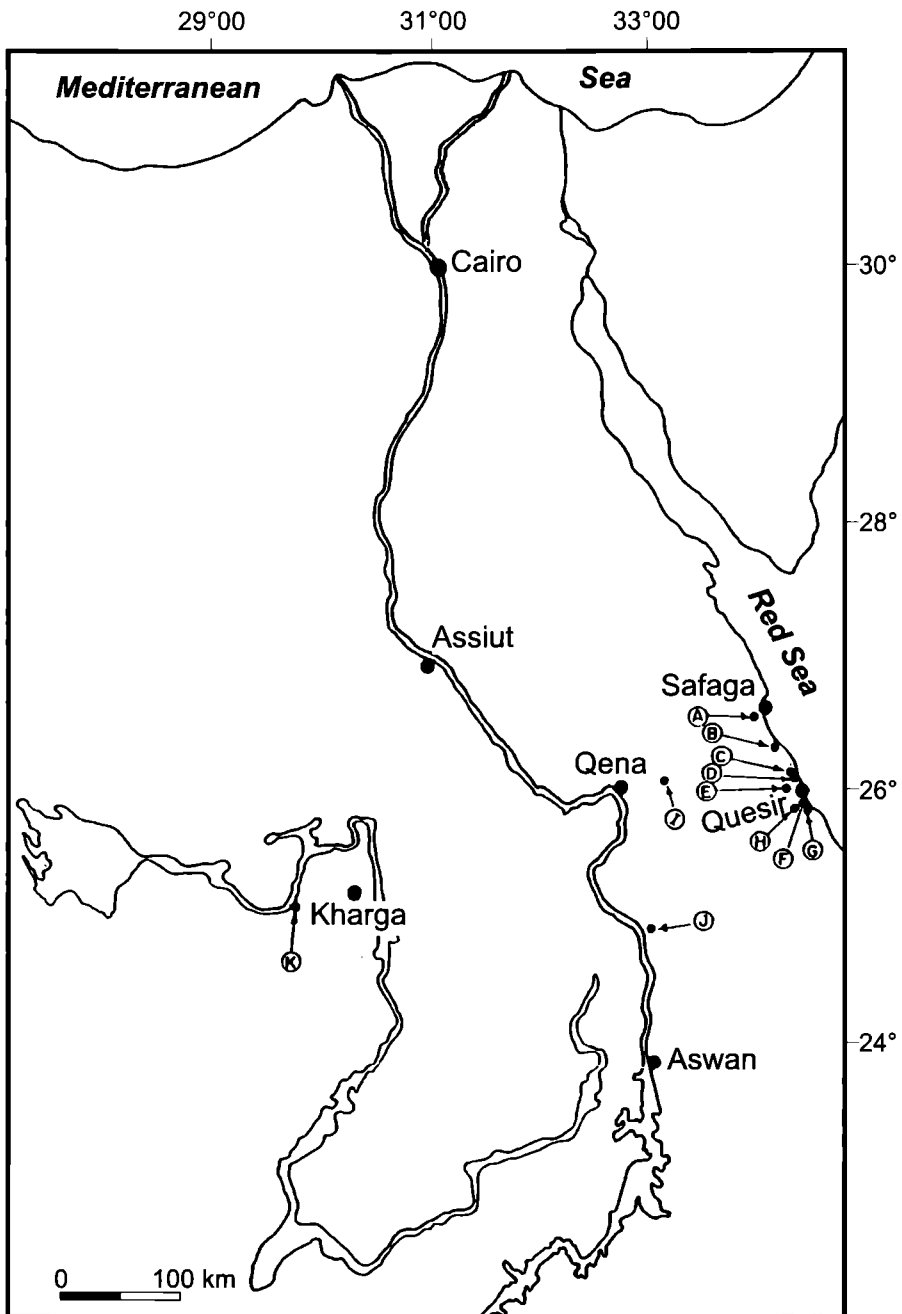


Fig. 1: Location map of investigated phosphorites. A – km 13 Safaga – Qena, B – Wadi Queh, C – north Yunis, D – Yunis, E – G. Anz (Galal Mine), F – Um Resifa, G – Zug El Bohar, H – Atshan, I – G. Qreiya, J – Abu Sabun, K – Abu Tartur.

ABDALLAH et al. 1972; EL KAMMAR, 1974; PHILOBBOS, 1976; ABDEL GAWAD, 1980; AHMED, 1983, 1988; SOLIMAN et al., 1986; GERMANN et al., 1987; GLENN, 1990)

The genesis of the Egyptian phosphorites however, remains obscure. Three scenarios have been suggested:

- (1) Direct precipitation from upwelling or pore waters (EL-TARABILI, 1969; PHILOBBOS, 1969 and SOLIMAN & AMER, 1972).
- (2) Biochemical processes (YOUSSEF, 1965)
- (3) Formation by means of microbial mediation (AHMED, 1988, 1995).

The purpose of this work is to present evidence of the role of microbial mediation in the genesis of Egyptian phosphorites stretching from the Red Sea into the Western Desert (Fig. 1).

## 2. GEOLOGICAL SETTING

The phosphorite-bearing sediments (siliciclastics and/or carbonates) in Egypt span the period from the Campanian to the Ypresian and have been subdivided into four main phosphogenic events (Table 1). This work deals with the Campanian-Maastrichtian phosphogenic events (Ph. E<sub>1</sub> – Ph. E<sub>2</sub>).

The first phosphogenic event (Ph. E<sub>1</sub>) developed mainly in a dense siliciclastic sequence (shales and siltstones, Quseir Shale) which is well exposed in the Eastern Desert and the Nile Valley areas. No marked variation in the lithofacies of the host sediments between the two areas exists.

The sediments of the Duwi Formation overlie conformably the Campanian marginal marine shales (Quseir Shale, SAID, 1962) and underlie deeper water shales and marls of the Maastrichtian Dakhla Formation (SOLIMAN et al., 1986). Most of the economically exploited phosphorite beds of Egypt are confined to the Duwi Formation (Ph. E<sub>2</sub>). Generally, the Duwi Formation consists of shales, siltstones, phosphatic sandstones, marls, phosphatic marls, oyster limestones, chert, porcellanite, glaucony and phosphorite beds of variable thickness (Fig. 2). A marked variation in the lithofacies of the Duwi Formation between the Red Sea, Nile Valley and Western Desert areas or even in the same area is noticed (Fig. 2). Oyster limestones are for example, frequently intercalated within the Duwi Formation of the Red Sea area whereas, glauconies are encountered interbedded in the phosphorite sequence of the Western Desert. Glauconies occur either as distinct horizons or intermingled with phosphorites (Pl. 1). Locally in the Red Sea area, the phosphorite-bearing sediments vary in both N-S and E-W directions. At Gabal Duwi (Quseir area) thick horizons (~2 m) of intact big oysters, up to 20 cm, are well developed and progressively decrease in thickness and size northwards, southwards and westwards. At the northern limit of the Duwi Formation (km 13 Safaga-Qena road) no oyster limestone is recorded. Again, southwards from Gabal Duwi to the Zug El Bohar area, the thickness of the oyster limestone beds decreases and the size of the oysters diminishes to 5 cm.

Large-scale or even small-scale synsedimentary deformations are frequently observed in the phosphorite-bearing sediments. The former were reported by HENDRICKS & LUGER (1987). Bending of clay laminae around some of the phosphate nodules is seen, which may indicate that these nodules were hard at the time of compaction.

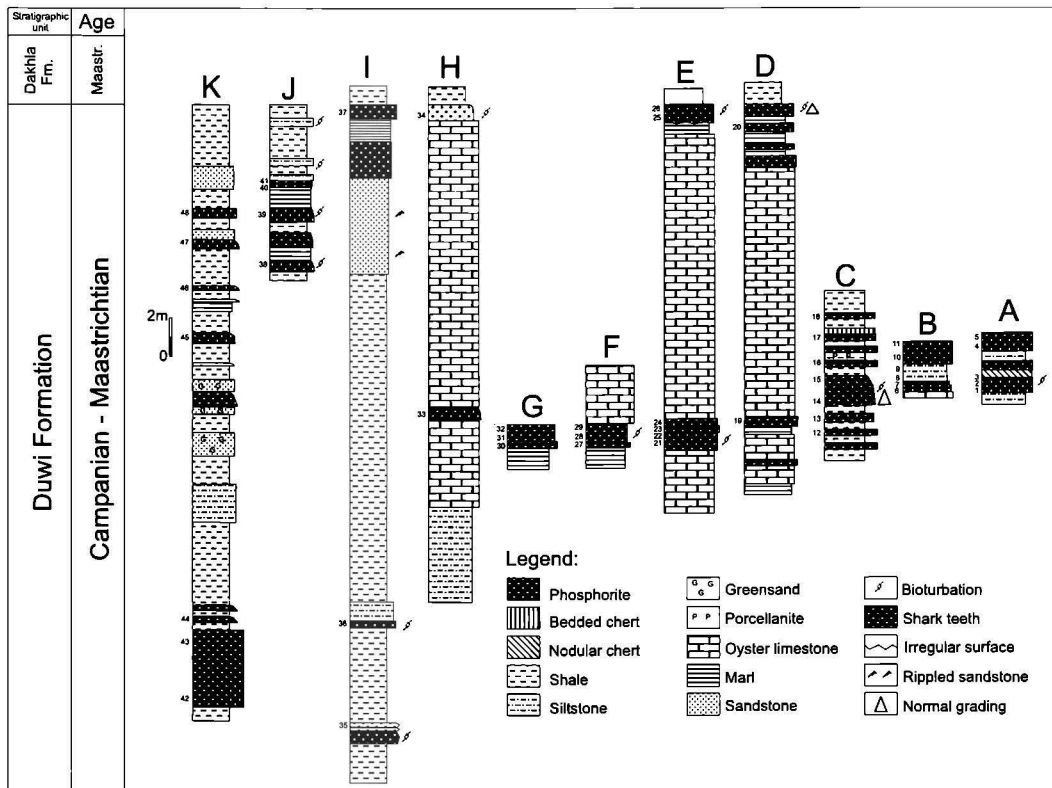


Fig. 2: Measured columnar sections.

Small and large-scale cyclicity of sedimentation units (a few centimeters to a few meters), bioturbation, normal grading and shallow basal scour are the most common features encountered in the phosphorite beds. Bioturbation represents episodic periods of bottom-water oxygenation within otherwise dysaerobic to anoxic conditions (GLENN & ARTHUR, 1990). Splitting phenomena and hummocky cross-bedding are observed in the phosphorites of Gabal Duwi and Abu Tartur areas respectively. The features recorded above may point to the accumulation of the examined phosphorites mainly by storm-induced events (tempestites) (e.g. AHMED, 1988, 1995).

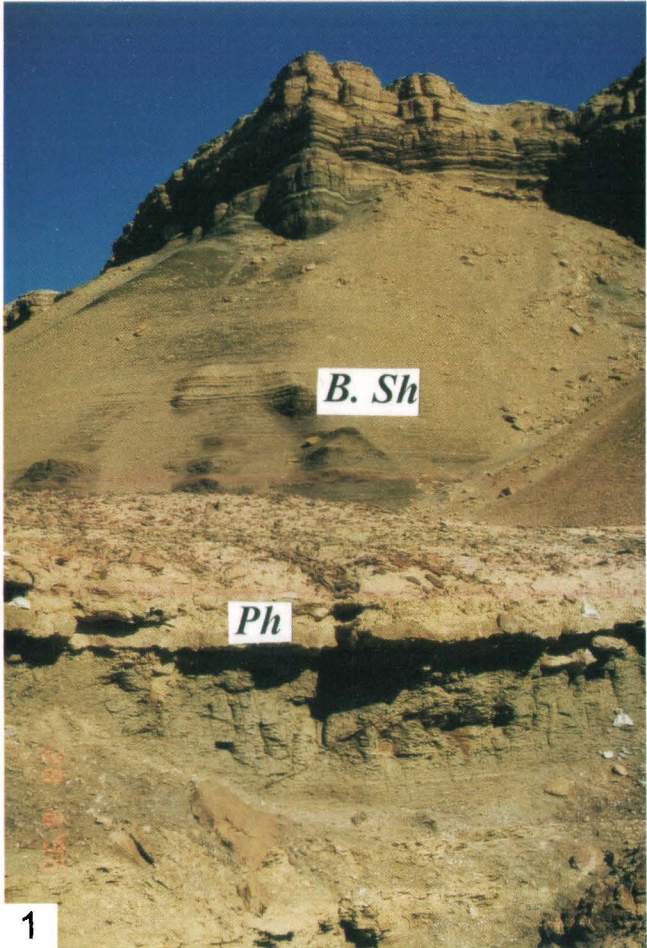
### Plate 1

Field photographs

Fig. 1: Phosphorites (Ph) intercalated in siliciclastic Black shale (B.Sh) facies, Gabal Qreiya

Fig. 2: Bedded glaucony facies, Abu Tartur area

Fig. 3: Intermingled glaucony-phosphorite horizon, Abu Tartur area



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### 3. MATERIALS AND METHODS

Representative phosphorite samples, in particular, the economic ones, from the Safaga area (km 13 Safaga-Qena road), the Quseir area (Wadi Queh, North Yunis, Yunis, Gabal Anz, Um Resifa, Zug El Bohar and Atshan), the Eastern Desert (Gabal Qreiya), the Nile Valley (Abu Sabun) and of the Western Desert (Abu Tartur) were collected for the present study.

Freshly fractured and thin-sectioned phosphorites were examined using SEM at Assiut University and at the Institute of Silicate Chemistry and Archaeometry, University of Applied Arts, Vienna.

SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> and CaO contents of fossilized diatom frustules were analyzed using an Energy Dispersive X-ray analyzer (EDX) coupled to a SEM Jeol-5400 Lv at Assiut University.

Powdered phosphorite samples (< 250 mesh) were investigated by X-ray diffraction techniques to determine their mineralogy. The method of GULBRANDSEN (1970) was used to determine the structural CO<sub>2</sub> content of the carbonate-fluorapatite (CFA).

In order to study the major oxide and the trace element geochemistry, the powdered phosphorite samples were analyzed using the X-ray fluorescence technique. Microprobe analyses of carbonate-fluorapatite (CFA) pellets and intraclasts were also carried out to establish their main major oxide composition. XRD, XRF and microprobe analyses were carried out at the Institute of Petrology, University of Vienna.

Phosphogenic Event	Litho-stratigraphic unit	Facies	Age	Distribution
Ph. E <sub>4</sub>	Thebes Formation	Phosphatic beds embedded in limestone, marl and chert	Ypresian	Eastern Desert and Nile Valley
Ph. E <sub>3</sub>	Dakhla Formation	Phosphorites and phosphatic beds included within grey fossiliferous shale	Maastrichtian-Danian	Eastern Desert, Nile Valley and Western Desert
Ph. E <sub>2</sub>	Duwi Formation	Phosphorites interbedded with oyster limestone, marl, chert, glaucony, black shale and sandstone	Campanian-Maastrichtian	Eastern Desert, Nile Valley and Western Desert
Ph. E <sub>1</sub>	Quseir Shale	Phosphorites included in variegated shales, sandy shales and siltstones	Campanian	Eastern Desert and Nile valley

Tab. 1: Phosphogenic events in Egypt. Age according to SAID (1962), ISSAWI (1972) and BARAKAT & EL DAWOODY (1973).

## 4. RESULTS AND DISCUSSIONS

### 4.1. Ultrastructures

Non-phosphatized fossil micro-organisms, phosphatized grains with tubular structures, phosphatized diatoms and crystallized apatite are the ultrastructures encountered in the freshly fractured and thin-sectioned samples.

#### 4.1.1. *Non-phosphatized fossil micro-organisms*

They are represented by branched or unbranched filamentous micro-organisms. These features are recorded in the examined phosphorite samples of the Yunis and Abu Tartur areas. In this context, it is worth mentioning that AHMED (1995) pointed to the existence of continental pollen and spores in some phosphorite nodules and silicified wood fragments in some phosphorites at the Zug El Bohar locality, Red Sea. A collective result may point to the active participation of continental influx during phosphogenesis (e.g. AHMED, 1995).

Very rare planktonic foraminifera were found in the matrix of the scanned productive phosphorites of the Abu Tartur area.

#### 4.1.2. *Apatite globules*

Apatite globules, 1  $\mu\text{m}$  in diameter, were observed in some of the phosphate samples of the Quseir area (Pl. 2, Fig. 1). They occur either as separate globules or as accumulations of globules. BIGNOT (1980), ZANIN et al. (1985) and SOUDRY & LEWY (1988, 1990) interpreted such structures as phosphatized cocci bacteria. ZANIN et al. (1985) reported that bacteria themselves actively assimilate P in the process of vital functions contributing finally to its concentration.

Ball-like ultrastructures ranging from 2 to 5  $\mu\text{m}$  in diameter have been recorded in the phosphorites of the Quseir area (Wadi Queh) (Pl. 2). ZANIN et al. (1985) attributed such structures found in the Cretaceous phosphorites of the East-European platform, the former USSR, and the Paleocene of Morocco to bacterial remains. In this respect it is worth mentioning that mineralized bacterial structures in phosphorites were first recorded by CAYEUX (1936) from France, North Africa and the USA. Many scientists (e.g. BATURIN, 1982; SOUTHGATE, 1986) explained the importance of bacteria in the degradation of planktonic organic matter and its consequent role in the contribution of some phosphorus to the pore water.

#### 4.1.3. *Phosphatized grains with tubular structures*

Bunches of phosphate tubules have been found within some of the CFA grains (Pl. 3). These tubules are open and display no preferential arrangement. In others, such structures are masked by CFA aggregates. They occur as empty holes, varying between 4 and 15  $\mu\text{m}$  in diameter (Pl. 3). Some of these holes are filled with globules of CFA reaching 5  $\mu\text{m}$  in diameter. Recrystallization and/or total filling in most cases has altered the cylindrical structures of these microbial entities, so that they are hard to recognize (e.g.

BRÉHÉRET, 1991). Such features indicate that mineralization processes were very rapid and that rigid forms were produced before any compaction (e.g. SOUDRY, 1987). Electron microprobe analysis of such structures has revealed that they contain 32%  $P_2O_5$ . These ultrastructures are similar to those encountered in the phosphatic concretions of France and interpreted by BRÉHÉRET (1991) as fungal hyphae.

#### 4.1.4. Phosphatized diatoms

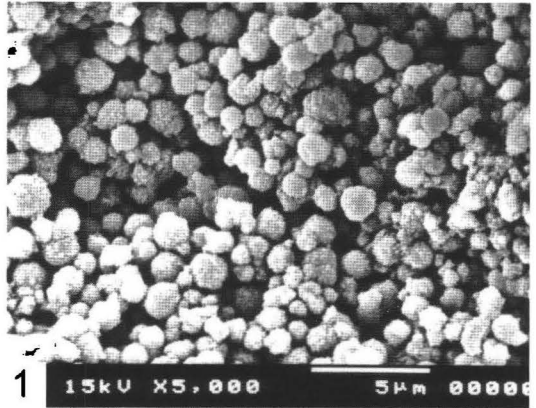
Concentric and pinnate marine diatom frustules (Pl. 4) were found in some of the investigated phosphorite particles especially those collected from the Red Sea area. The concentric type is more common. EDX analysis demonstrates that the degree of phosphatization of the diatom frustules is variable but in most cases nearly complete. LAMBOY (1990) attributed the phosphatized diatoms from the Peruvian continental margin to phosphatic mouldings aided by bacteria rather than to real molecule by molecule substitution of silica by apatite. In some cases the diatom frustules are dissolved and the remaining parts are filled by aggregates of CFA of approximately  $1 \times 2 \mu\text{m}$ .

The phosphorites forming at present days off the coast of Peru, Chile and southwest Africa are known to be associated with diatomaceous oozes where upwelling currents prevail (BURNETT, 1977; PRICE & CLAVERT, 1978; BIRCH, 1979). According to PERES & DEVENZE (1964), diatoms have the ability to fix the phosphorus of sea water and, after their decay, can be considered the source of P to sediments. EDX results show that most of the examined diatom frustules contain relatively higher  $P_2O_5$  values than their ground-mass, an observation in accordance with BURNETT (1977), who reported that diatoms are important sites for the growth of apatite. BERNER (1969) added that the decomposition of diatoms causes a rise in pH because of the formation of  $NH_4^+$  and other nitrogenous compounds, where in such conditions apatite could be precipitated (ROBERSON, 1966; PYTHOWICZ & KESTER, 1967). LAMBOY (1990) mentioned that the dissolution of diatom frustules creates a new porosity which is sometimes utilized for apatite growth.

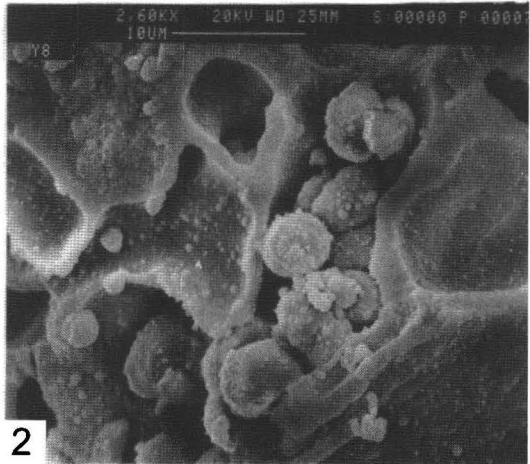
As mentioned before, there is a remarkable variation in the phosphorite-bearing sediments of the Duwi Formation of the Eastern Desert, the Nile Valley and the Western Desert. The obtained results show the importance of diatoms in the understanding of chert-phosphorite occurrences in the Duwi Formation of the Eastern Desert and Nile Valley which are typical of many phosphorite deposits world wide.

GERMANN et al. (1987) reported that the lack of chert in the Duwi Formation of the Western Desert may be attributed either to the absence of silica-producing planktonic organisms or the consuming of biogenic silica by the neof ormation of Fe-rich smectites. SEM investigation of Abu Tartur phosphorites has revealed that they contain diatom frustules. Therefore, the lack of chert cannot be attributed to the absence of silica-producing organisms. In our opinion, the silica resulting from the dissolution of diatoms may have been consumed to form the widespread glaucony facies associated with the phosphorites in the Abu Tartur area.

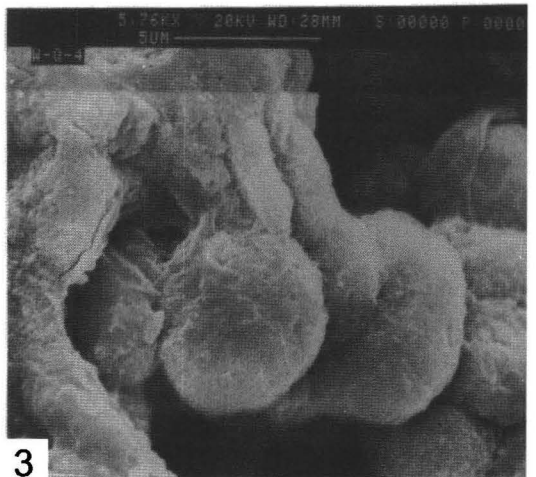




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**Plate 2**

SEM photomicrographs

Fig. 1: Apatite globules

Fig. 2: Globular CFA grains formed in the hollow spaces

Fig. 3: Phosphatized balls (algae?)

#### 4.1.5. Crystallized apatite

Apatite crystals are usually developed in microholes and tubular structures or along the fractures crossing the colophane (peloids or intraclasts) or filling moulds of previous (dissolved) diatom frustules. They range between 5 and 50  $\mu\text{m}$  in size. Such observation may point to their formation in the secondary diagenetic phosphatization phase.

### 4.2. Mineralogy

The mineralogy of the phosphorites was determined by using the X-ray diffraction technique. The structural  $\text{CO}_2$  of CFA was calculated according to the equation of GULBRANDSEN (1970).

The obtained data have revealed that carbonate-fluorapatite (CAF) is the only phosphate mineral encountered in the investigated samples. Bock (1986) mentioned that Fe-phosphates such as leucophosphorite and phosphosiderite have been detected in the strongly weathered outcrops of northern Kharga.

Quartz, calcite, dolomite, gypsum, anhydrite, halite and clays are also encountered in variable percentages. With the exception of dolomite, which was recorded from the phosphorites of the Eastern Desert and the Western Desert, the identified minerals have not revealed any noticeable trend. Pyrite cubes or disseminated ones are frequently encountered in the phosphorite-bearing siliciclastics, either in the groundmass or in their particles respectively.

Structural  $\text{CO}_2$  content varies in the studied samples from 1.7 to 5.8%. The highest value was obtained from the phosphorite samples at km 13 Safaga-Qena road and the Wadi Queh area, whereas the lowest one was encountered in the phosphorite samples of the Zug El Bohar area. The studied carbonate-fluorapatites are distinguished here based on their average structural  $\text{CO}_2$  contents into high, medium and low substituted

### Plate 3

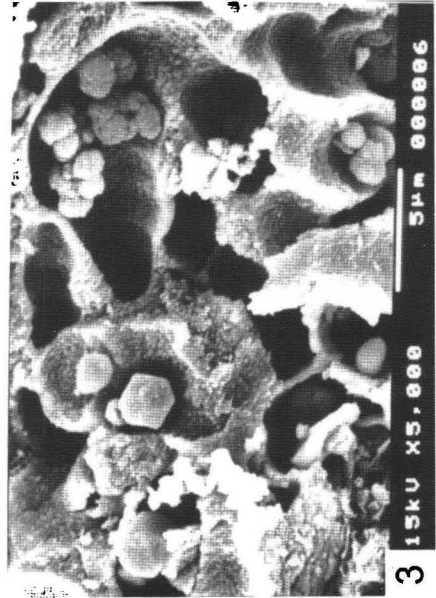
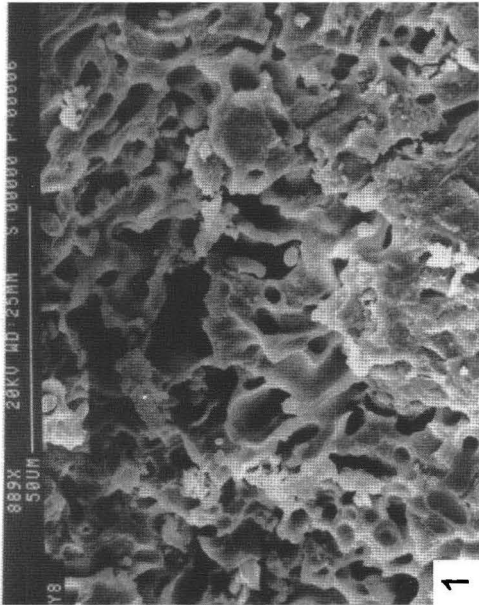
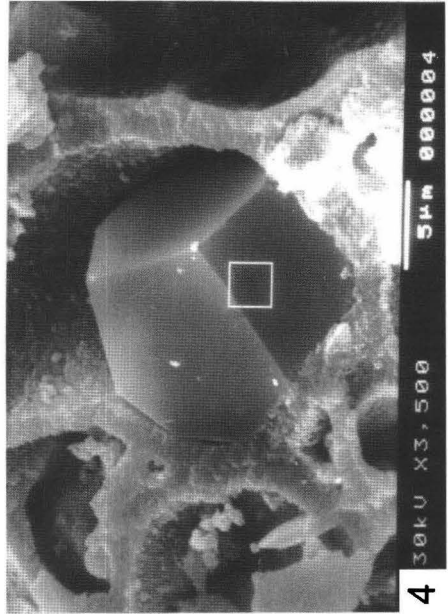
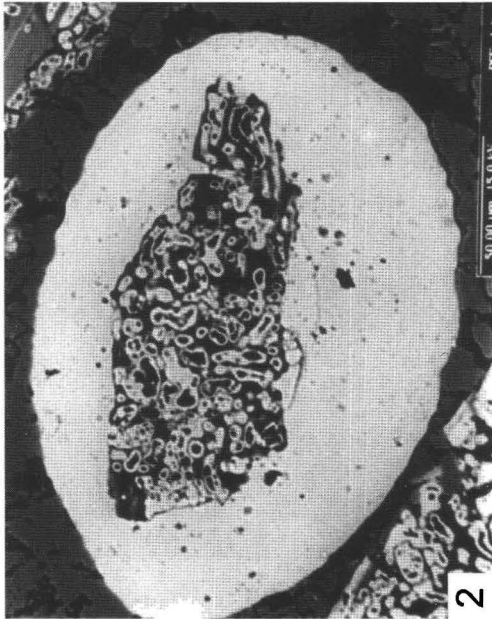
SEM photomicrographs

Fig. 1: Tubular structures within CFA grains

Fig. 2: Tubular structures in the core of a CFA pellet

Fig. 3: Globular CFA grains filling tubular structures

Fig. 4: Calcite crystals filling the tubular structures



varieties. The high substituted varieties contain 4.5-5.2% structural CO<sub>2</sub> and are represented by the phosphorites at km 13 Safaga-Qena road; Wadi Queh and Gabal Qreiya. The medium substituted types, however, contain 3–4.4% structural CO<sub>2</sub> and are represented by the phosphorites collected from Yunis, Gabal Anz, Um Resifa and Abu Tartur. The low substituted varieties, which contain <3% CO<sub>2</sub>%, are represented by phosphorites sampled from the Zug El Bohar and Atshan areas. GULBRANDSEN (1970) attributed the variations in the CO<sub>2</sub> content in the Phosphoria Formation to environmental changes during sedimentation. This result disagrees with the present findings, where no noticeable trend was observed in the CO<sub>2</sub> -content with facies variation. For example, some of the phosphorite samples intercalated in a siliciclastic facies (e.g. Gabal Qreiya and Abu Tartur, Fig. 2) contain up to 5.7% structural CO<sub>2</sub>, unlike those intercalated in carbonate facies (e.g. Gabal Anz), which contain 1.7%. In any given phosphorite bed, the structural CO<sub>2</sub> content decreases upward as the grain size decreases (fining upward). This may be attributed to the effect of reworking and/or weathering prevailing during or after phosphogenesis (e.g. AHMED, 1995). Our results agree with those of NATHAN et al. (1990), who mentioned that the phosphorite samples with coarser grains have a significantly higher CO<sub>2</sub> content than the fine-grained ones. They attributed such variation to epigenesis and/or weathering effects.

According to the calculations carried out by McCLELLAN & LEHR (1969), the  $a_0$  cell dimension of the carbonate-fluorapatite in our samples was found to range between 9.320 Å and 9.357 Å. According to ALTSCHULER et al. (1952), these values are related to the carbonate-fluorapatite phase.

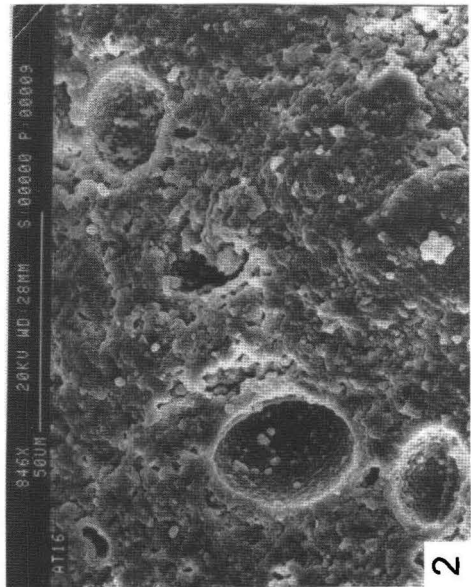
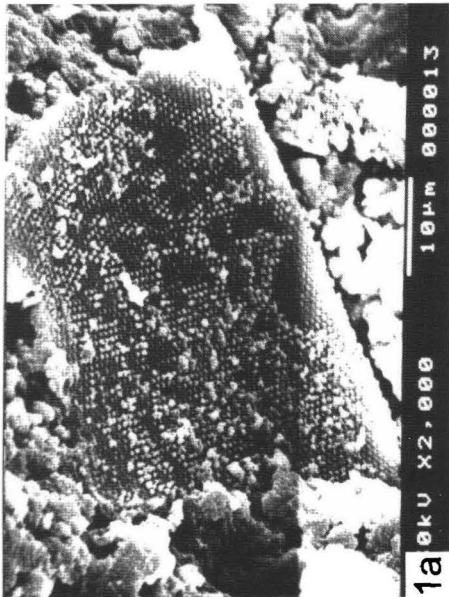
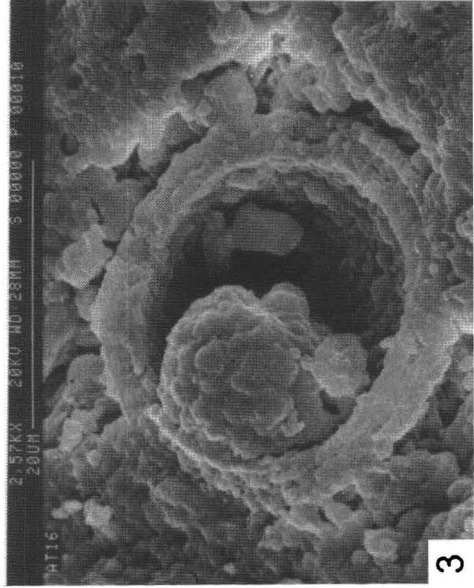
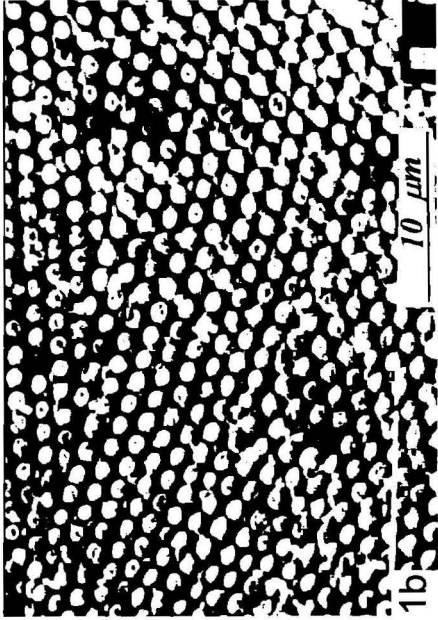
#### Plate 4

SEM photomicrographs

Fig. 1a, 1b: Diatom frustules, Zug El Bohar and Yunis area respectively

Fig. 2: Diatom skeletons, Abu Tartur phosphorites

Fig. 3: Partial dissolution of diatom frustules filled with microcrystalline CFA, Abu Tartur phosphorites



Area/sample Oxides/ Element (%)	Eastern Desert					Western Desert	
	Yunis	Gabal Anz		Gabal Qreiya		Abu Tartur	
	16(18)	21(20)	25(36)	32(20)	35(44)	42(27)	46(20)
SiO <sub>2</sub>	0.56	0.08	0.23	0.04	0.55	0.17	0.02
Al <sub>2</sub> O <sub>3</sub>	0.01	0.03	0.08	0.09	0.18	0.04	0.58
K <sub>2</sub> O	0.01	0.01	0.02	0.03	0.05	0.01	0.03
Na <sub>2</sub> O	1.68	0.47	0.47	0.76	0.78	0.62	0.48
MgO	0.25	0.16	0.17	0.28	0.66	0.11	0.40
FeO	1.72	0.54	0.12	2.48	2.01	1.08	1.52
CaO	48.99	51.61	53.03	50.69	48.36	50.85	47.69
P <sub>2</sub> O <sub>5</sub>	27.64	31.04	30.59	30.04	27.32	29.19	31.31
F	2.52	4.17	4.46	3.59	2.84	3.51	3.78
Cl	0.09	0.07	0.12	0.14	0.15	0.16	0.15
F/P <sub>2</sub> O <sub>5</sub> ratio	0.091	0.13	0.15	0.12	0.10	0.12	0.12

Note: Total iron represented as FeO. Number of analyzed points are given in brackets

Table 2: Average microprobe analysis of carbonate-fluorapatite

### 4.3. Francolite chemistry

SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Na<sub>2</sub>O, MgO, FeO, CaO, P<sub>2</sub>O<sub>5</sub>, F and Cl were determined in the studied francolites (Table 2) by using a Cameca Sx 100 microprobe. K<sub>α</sub> lines were measured at 15 KV and 20μA. The analyzed samples represent phosphorite-bearing siliciclastics (samples 16, 32, 35, 42 and 46) and phosphorite-bearing carbonates (samples 21, 25) (Fig. 2). Table 2 shows a noticeable variation in the chemistry of the carbonate-fluorapatite between the two facies. FeO, MgO and Na<sub>2</sub>O are relatively higher in the francolite of the phosphorite-bearing siliciclastic facies. CaO, F and the F/P<sub>2</sub>O<sub>5</sub> weight ratio are, however, relatively enriched in the francolites of the phosphorite-bearing carbonates. Moreover, there is a marked variation in the chemistry of francolites, in particular SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, CaO, P<sub>2</sub>O<sub>5</sub> and MgO, from the same facies (Table 2, Fig. 2) which may result from the weathering and reworking effects, the grain size of the phosphate particles and an abundance of micro-organisms (e.g. AHMED, 1995).

### 4.4. Phosphorite samples chemistry

The studied phosphorite samples were analyzed for their major oxide and trace element content (Table 3) by using the X-ray fluorescence technique. In order to evaluate the behaviour of trace elements, the analyzed phosphorite samples are grouped here into:

- (1) High-grade phosphorites (>30% P<sub>2</sub>O<sub>5</sub>).
- (2) Medium-grade phosphorites (30-20% P<sub>2</sub>O<sub>5</sub>).
- (3) Low-grade phosphorites (< 20% P<sub>2</sub>O<sub>5</sub>).

Table 3 shows that the high grade phosphorites represent 6.25% of the analyzed samples, whereas the medium grade and low grade phosphorites constitute 64.58 and 29.17% of the analyzed samples respectively. A marked increase in the averages of total trace elements ( $\Sigma$  trace elements) with an increasing grade of phosphorites was noticed (Table 4).

The high-grade phosphorites contain a relatively higher content of trace elements (1862 ppm). This value diminishes, with decreasing  $P_2O_5$  content, to 1606 ppm in the low-grade phosphorites.

Therefore, the obtained results could be differentiated into: (1) Trace elements enriched in the studied marine phosphorites include Sr, Pb, Cr, Y and Ba. ALTSCHULER (1980) pointed out that Sr, Pb and Y are generally more concentrated in purified marine apatite than in impure phosphorites. KRAUSKOPF (1956) and GULBRANDSEN (1969) attributed the enrichment in Cu, Cr and Ba of marine phosphorites to organic complexing. (2) Trace elements depleted in phosphorites. The low-grade phosphorites, in contrast, contain a relatively high concentration of Zr, Rb, Zn, Ni and V (Table 4). These elements are not accommodated in the apatite structure. Their behaviour is controlled by the detrital influx (heavy minerals and/or clay minerals) (e.g. AHMED, 1995).

Locally, the content of trace elements varies in phosphorites of the same grade. For example, the high grade phosphorites of the Quseir area contain a relatively high trace element content compared with those of Safaga area (Table 3). Moreover, the medium grade phosphorites of Abu Tartur are the richest one in trace element content compared with those of the Eastern Desert or the Nile Valley. Such local variation in trace element enrichment or depletion may be controlled in principle by facies control (siliciclastic or carbonate) (e.g. EL HADDAD & AHMED, 1991; AHMED, 1995). In this context, it is worth mentioning that AHMED (1995) attributed the variation in trace element content of the phosphorites of the Red Sea area to the grain size of the phosphate particles and to the existence of micro-organisms.

Comparison of the analyzed samples, in particular the high-grade phosphorites, with the results reached by ALTSCHULER (1980) (Table 4) led to the following conclusions:

- (1) Sr, Ga and Cr are relatively enriched in the studied samples.
- (2) Zr, Y, Pb, Cu, Ni, Sc, V, Ba and La are relatively depleted.

The deviation from the results of ALTSCHULER (1980) may be attributed to variations in the nature of phosphorite components (i.e. peloids or intraclasts), grain size of phosphorite components and facies control (i.e., siliciclastics or carbonates).

		Eastern Desert																
		Km. 13 Safaga-Qena					Wadi Queh						North Yunis					
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	
SiO <sub>2</sub>	%	2.56	1.29	27.06	1.52	12.15	10.70	2.73	22.73	2.39	2.70	5.50	23.85	19.20	17.30	13.50	44.20	
Al <sub>2</sub> O <sub>3</sub>		1.58	0.13	0.07	0.58	5.00	0.66	0.28	–	0.43	0.68	0.26	0.28	0.19	0.20	2.10	0.09	
CaO		50.24	52.96	36.08	75.97	55.39	45.47	52.67	38.52	54.07	53.36	50.70	36.69	40.07	41.62	43.60	24.60	
MgO		0.60	0.48	0.36	0.69	1.14	2.10	11.37	0.26	4.60	3.50	0.44	1.10	0.27	0.27	0.65	1.30	
Na <sub>2</sub> O		1.51	1.55	1.30	0.95	1.01	0.81	1.35	0.95	1.03	1.20	1.33	1.90	1.10	1.10	1.25	–	
K <sub>2</sub> O		–	–	–	–	0.57	0.05	–	–	0.06	–	–	–	–	–	–	0.10	–
P <sub>2</sub> O <sub>5</sub>		30.46	31.71	26.22	7.37	11.23	25.20	17.32	29.80	26.20	27.60	30.88	26.72	29.70	29.36	27.20	20.10	
Fe <sub>2</sub> O <sub>3</sub>		0.37	0.15	0.38	0.59	1.26	0.30	1.27	–	0.52	1.15	0.18	0.58	1.70	1.20	1.90	0.80	
F		4.36	4.10	3.60	1.58	1.92	3.57	2.48	3.60	3.45	3.40	3.80	2.88	3.02	3.30	3.00	2.50	
Cl		1.08	1.02	0.95	0.40	0.03	–	0.67	–	0.05	0.12	0.06	0.90	0.07	0.05	0.10	0.50	
S		0.65	0.84	0.83	0.67	0.61	0.19	0.44	0.54	0.58	0.70	0.73	0.92	0.60	0.70	0.80	0.70	
Nb		(ppm)	2	2	2	2	4	3	1	3	3	4	4	2	2	3	3	2
Zr			1	9	2	4	21	12	6	6	9	7	11	14	12	9	19	11
Y			27	64	20	43	101	27	10	22	91	121	143	56	104	99	112	159
Sr	738		1382	696	1168	1021	877	518	781	952	1312	1288	727	1128	1689	1024	779	
Rb	3		11	3	8	15	9	3	5	9	12	12	5	6	9	11	3	
Pb	1		68	19	57	14	20	7	15	33	40	37	8	11	17	17	8	
Ga	3		6	3	5	6	4	1	4	4	6	7	3	5	8	7	4	
Zn	117		187	90	323	206	162	189	52	270	632	149	53	50	99	85	27	
Cu	7		10	3	6	22	9	16	22	16	25	13	7	5	6	5	11	
Ni	28		27	11	23	61	8	10	8	29	61	26	17	20	21	22	22	
Co	6		6	5	4	6	6	5	4	4	7	6	9	12	7	5	14	
Sc	2		4	5	1	3	1	1	5	4	2	1	9	9	10	9	12	
Cr	324		109	253	72	174	133	65	90	27	105	89	145	122	125	60	351	
V	31		117	42	91	81	85	79	37	96	117	59	46	23	41	78	29	
Ba	276		89	14	33	63	48	17	1	34	55	24	49	134	116	125	196	
La	18		33	17	27	46	12	14	15	31	39	39	46	73	63	57	148	

Tab. 3: Results of chemical analysis; – not determined Fe<sub>2</sub>O<sub>3</sub> = total iron



		Eastern Desert															
				Yunis		Gabal Anz						Um Reisfa			Zug El Bohar		
		17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
SiO <sub>2</sub>	%	38.24	32.00	2.00	26.10	2.45	7.60	37.56	4.10	1.90	3.92	26.90	26.16	23.31	26.07	7.98	4.67
Al <sub>2</sub> O <sub>3</sub>		3.80	2.68	0.30	4.45	0.20	0.35	0.10	0.09	0.50	0.36	0.24	0.37	0.31	-	0.45	0.20
CaO		27.90	32.23	50.31	30.44	50.88	48.13	31.64	48.80	49.38	49.02	33.54	36.73	38.91	36.88	54.52	49.56
MgO		0.87	0.80	2.25	1.70	0.65	0.45	0.20	3.02	2.64	1.85	0.70	0.68	0.23	0.33	6.50	1.43
Na <sub>2</sub> O		0.95	1.10	1.00	1.16	1.20	1.25	0.75	1.11	2.71	2.08	4.03	1.78	1.08	1.36	0.75	1.00
K <sub>2</sub> O		0.25	0.16	-	0.40	-	-	-	-	0.05	-	0.07	0.09	-	-	-	-
P <sub>2</sub> O <sub>5</sub>		18.00	19.81	25.59	17.07	21.25	29.64	24.00	25.20	26.76	27.64	24.20	25.68	28.85	27.02	24.93	28.22
Fe <sub>2</sub> O <sub>3</sub>		1.45	0.90	0.10	1.21	1.40	1.10	0.50	1.08	0.60	0.06	0.25	0.11	0.09	0.34	0.88	0.43
F		2.10	1.90	3.57	2.12	2.75	3.54	2.79	3.55	3.43	3.69	2.62	3.11	3.56	2.94	3.05	3.35
Cl		0.10	0.14	0.10	0.70	1.94	0.60	0.25	0.33	1.55	1.02	2.95	0.92	0.17	0.58	-	0.06
S		0.56	0.58	0.50	2.66	7.9	0.97	0.64	0.64	0.67	0.73	0.72	0.82	0.56	0.66	0.43	0.59
Nb		(ppm)	2	3	2	5	2	3	3	1	2	2	2	2	3	3	2
Zr	30		15	10	16	12	8	1	6	13	6	1	2	1	1	10	7
Y	107		41	19	32	60	87	48	22	54	104	12	15	22	11	33	58
Sr	653		896	943	1159	1076	1107	831	523	1155	1455	897	1046	1081	1005	786	1240
Rb	9		9	9	24	8	11	5	5	10	10	5	7	7	5	51	11
Pb	5		9	15	27	60	19	6	6	18	16	10	34	28	16	72	103
Ga	6		6	4	10	5	5	2	1	6	7	4	4	5	4	3	6
Zn	67		65	95	310	101	113	164	102	200	119	230	199	118	201	336	394
Cu	2		6	2	16	7	12	10	7	14	31	2	4	3	4	3	4
Ni	24		23	4	43	16	19	18	23	26	45	7	4	5	9	14	12
Co	7		8	5	7	6	7	6	4	6	5	5	7	5	6	6	6
Sc	10		9	1	2	5	2	3	10	4	3	3	1	3	1	2	2
Cr	129		81	73	82	69	92	290	43	58	90	205	109	122	291	85	76
V	108		75	27	62	81	120	74	55	65	28	31	67	41	59	84	58
Ba	112		36	5	217	45	72	92	27	292	461	24	130	44	110	81	89
La	87		22	10	9	36	34	24	8	24	49	14	11	14	10	26	32

Tab. 3: continued.

							Nile Valley				Western Desert						
		Atshan		Gabal Qreiya			Abu Sabun				Abu Tartur						
		33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
<b>SiO<sub>2</sub></b>	%	24.48	5.27	17.96	9.78	52.80	24.91	16.74	17.39	27.20	2.22	7.16	13.25	24.81	16.40	9.69	6.47
<b>Al<sub>2</sub>O<sub>3</sub></b>		0.76	1.00	0.92	1.78	0.33	1.54	0.10	0.46	0.84	0.64	1.70	2.36	2.46	1.00	1.58	2.87
<b>CaO</b>		39.19	45.37	50.43	55.65	21.90	33.80	45.05	39.81	37.38	54.76	43.61	42.33	36.69	37.88	39.90	46.27
<b>MgO</b>		0.40	1.81	0.40	0.59	0.33	0.50	0.40	0.37	0.35	0.89	1.76	6.68	6.50	0.50	0.37	3.47
<b>Na<sub>2</sub>O</b>		0.62	1.13	1.08	1.00	0.80	0.84	1.16	1.30	0.60	1.70	0.96	0.63	0.50	0.79	0.35	0.80
<b>K<sub>2</sub>O</b>		0.08	0.10	0.06	0.09	–	0.07	0.05	0.05	0.06	0.05	0.15	0.10	0.39	0.15	0.78	0.20
<b>P<sub>2</sub>O<sub>5</sub></b>		21.35	24.10	17.78	13.50	16.50	23.88	21.38	25.65	23.81	26.46	21.84	11.92	8.73	22.23	4.80	16.89
<b>Fe<sub>2</sub>O<sub>3</sub></b>		0.97	2.34	1.50	2.35	0.55	1.47	0.60	2.19	1.15	0.93	2.55	2.98	4.48	2.86	7.50	4.61
<b>F</b>		2.38	2.70	1.82	1.27	1.95	2.57	2.34	2.97	2.76	3.68	2.02	1.62	1.01	2.37	–	2.18
<b>Cl</b>		0.12	0.30	0.24	0.45	0.36	0.06	0.70	1.59	0.10	0.76	0.45	1.22	0.08	0.09	0.09	0.45
<b>S</b>		0.40	4.50	1.16	4.49	1.43	0.55	1.75	0.50	0.32	1.15	6.65	3.43	4.07	4.67	21.67	3.84
<b>Nb</b>		(ppm)	3	2	3	3	3	2	3	2	3	2	2	1	1	2	2
<b>Zr</b>	30		31	11	8	3	23	3	8	8	7	34	18	19	12	20	14
<b>Y</b>	54		240	52	123	83	85	26	52	55	113	246	76	77	49	16	93
<b>Sr</b>	1180		1581	1079	1192	1264	918	1106	1359	1374	1566	1528	540	714	1014	502	819
<b>Rb</b>	9		12	10	11	11	8	6	9	10	12	13	3	13	11	9	8
<b>Pb</b>	129		36	22	26	20	17	11	15	17	91	37	3	17	13	8	8
<b>Ga</b>	6		8	5	6	5	5	4	7	7	7	8	2	5	6	5	4
<b>Zn</b>	223		282	362	526	238	263	88	149	120	495	60	84	95	349	25	138
<b>Cu</b>	7		15	12	22	10	16	4	12	11	17	16	4	12	12	6	13
<b>Ni</b>	18		50	39	40	29	67	6	16	20	37	14	45	81	18	6	40
<b>Co</b>	6		13	4	5	8	31	5	4	5	6	7	14	21	7	1	7
<b>Sc</b>	4		18	1	1	1	11	2	6	6	1	21	9	8	6	9	4
<b>Cr</b>	68		64	135	100	81	73	135	77	65	127	53	29	51	80	48	91
<b>V</b>	67		61	108	135	82	42	66	71	53	73	67	38	60	80	53	82
<b>Ba</b>	79		176	10	18	384	123	187	456	115	74	198	240	40	29	1	32
<b>La</b>	33		139	21	43	30	67	21	37	33	39	146	70	60	43	23	50

Tab. 3: continued.

Element	Average Phosphorites	High grade phosphorites > 30% P <sub>2</sub> O <sub>5</sub>			Medium grade phosphorites < 30-20% P <sub>2</sub> O <sub>5</sub>			Low grade phosphorites < 20% P <sub>2</sub> O <sub>5</sub>		
		Average conc.	Enrichment factor	Depletion factor	Average conc.	Enrichment factor	Depletion factor	Average conc.	Enrichment factor	Depletion factor
Nb	–	3	–	–	2	–	–	2	–	–
Zr	70	7	–	10	12	–	5.8	14	–	5.0
Y	260	78	–	3.3	75	–	3.5	63	–	4.1
Sr	750	1136	1.51	–	1089	1.5	–	932	1.2	–
Rb	–	9	–	–	9	–	–	11	–	–
Pb	50	35	–	1.4	28	–	1.8	21	–	2.4
Ga	4	5	1.3	–	5	1.3	–	5	1.3	–
Zn	195	151	–	1.3	175	–	1.1	210	1.1	–
Cu	75	10	–	7.5	10	–	7.5	12	–	6.3
Ni	53	27	–	2	21	–	2.5	34	–	1.6
Co	7	6	–	1.2	20	2.8	–	7	–	–
Sc	11	2	–	5.5	6	–	1.8	4	–	2.8
Cr	125	174	1.4	–	114	1.1	–	95	–	1.3
V	100	59	–	1.7	61	–	1.6	82	–	1.2
Ba	350	130	–	2.7	120	–	2.9	87	–	4
La	147	30	–	4.9	46	–	3.2	37	–	4
<b>Total</b>		1862			1793			1606		

Table 4: Average concentration of trace elements (ppm) in the studied samples compared with the average phosphorites of ALTSCHULER (1980).

## 5. PALEO GEOGRAPHIC SETTING AND PHOSPHOGENESIS

The genesis of ancient marine phosphorites is still a matter of global debate and controversy. Whether or not the phosphorites forming at present are representative of the ancient ones is a subject of discussion (BENTON, 1980; SHELDON, 1981; SOUDRY, 1987). Most scientists concluded that the development of phosphorites was related to productivity by the delivery of oceanic phosphate through coastal upwelling (e.g. EL TARABILI, 1969; GLENN & MANSOUR, 1979; SHELDON, 1981). KOLODNY (1980) pointed out that the formation of apatite in the recent phosphorite deposits of Chile, Peru and of south-west Africa represent present-day upwellings. This process is, however, not sufficient in most areas of present-day upwelling (KOLODNY, 1980). The average phosphate content of upwelling water is ~0.2 ppm (SPENCER, 1975). In our case the upwelling mechanism was not the only source of phosphorus. Transportation of phosphorus from the south of Egypt via fluvial processes from the intensively weathered platform can not be neglected (GLENN & ARTHUR, 1990), at a time when the climate of the Late Cretaceous was very humid and warm, as confirmed by the palynology of the Dakhla Formation (SCHRANK, 1984). Phosphorus was released to the Campanian-Maastrichtian Egyptian shelf from suspended sediments (e.g. POMEROY et al., 1965; GLENN & ARTHUR, 1990) or from phosphorus-bearing iron compounds (e.g. BERNER, 1973; DE LANGE, 1986).

The role of microbial mediation in phosphogenesis has been discussed by many scientists. BATURIN (1982) and others postulated that, in areas of modern phosphogenesis, the pore waters enriched in phosphate are due to the degradation of the organic matter of planktonics. A similar conclusion was reached by DAHANAYAKE & KRUMBEIN (1985) who postulated that microbial mats growing in shallow water environments play an important role as enriching and precipitating media during the formation of the phosphate deposits of Algeria. O'BRIEN & VEEH (1982) attributed the formation of the modern phosphate nodules from the eastern Australian margin to the assimilation of phosphate by bacteria from sea water. As mentioned before, phosphatized microorganisms (algae, bacteria and fungi) have been found in most of the examined phosphorite particles, therefore, the role of microorganisms in phosphorus concentration must be taken into consideration. In this respect, it is worth mentioning that REIMERS et al. (1990) reported that the filamentous bacteria (*Beggiatoa* spp) are able to assimilate large quantities of phosphorus. Accordingly, the growth of such microorganisms under an anoxic environment would appear to catalyse P mineralization near the sediment-water interface (e.g. BRÉHÉRET, 1991) and acts as a "phosphate pump" toward the underlying sediment (BURNETT & FROELICH, 1988). According to SOUDRY & SOUTHGATE (1989) the post-mortem phosphatization of bacterial populations, proliferating at the sediment-water interface, produces phosphatic layers which are later broken into nodules. The Egyptian phosphorites were accumulated in a restricted environment sheltered from the open marine by islands and shoals (GERMANN et al., 1987) or in a silled basins (GLENN & ARTHUR, 1990). These basins of phosphatic traps (SLANSKY, 1986) suggest a highly productive area with current winnowing along its flanks and downslope redeposition towards its center (e.g. GLENN & ARTHUR, 1990).

In conclusion, it seems that phosphogenesis starts with the microbial mat (algae, bacteria and fungi) forming a complex bottom-dwelling microbial community growing in a restricted marine environment which was partially able to fix phosphorus; the latter

being contributed either from upwelling or fluvial processes. SUESS (1988) considered the dissolution of fish debris as another potential source of P. In this context, it is worth mentioning that GLENN & ARTHUR (1990) attributed the relative reduced rates of structural  $\text{CO}_3^{2-}$  substitution in CFA in the Egyptian phosphorites to inorganic contributions of dissolved phosphate from the dissolution of fish debris. Dissolution of diatoms took place which led to the supersaturation of the pore water with silica, forming either chert and/or Porcellanite in association with phosphorites of the Eastern Desert and the Nile Valley, or the glauconites of the Abu Tartur area.

According to LAMBOY (1990), the dissolution of diatoms creates a new porosity which is favourable to apatite growth during the low energy event. Such result was demonstrated by the relative enrichment of  $\text{P}_2\text{O}_5$  in diatom frustules compared with the ground-mass.

The low energy event is preceded by a high energy event which prevailed during a regressive phase as evidenced by bioturbation, reworking and winnowing of the detritus leading to the upgrading of phosphorites. The mode of formation of Egyptian phosphorites is consistent with that of the Holocene seafloor phosphorite nodules of Peru, and Chile or the Neogene phosphorites of the Sea of Japan.

## 6. CONCLUSIONS

SEM investigation of freshly fractured and thin-sectioned phosphorite samples has revealed the presence of various ultrastructures in the Upper Cretaceous Egyptian phosphorites. Commonly encountered ultrastructures are non-phosphatized fossil micro-organisms, phosphatized grains with tubular structures, phosphatized diatoms and crystallized apatite.

The non-phosphatized particles may point to their transportation via fluvial processes prevailing during phosphogenesis. The phosphatized diatoms (diatom moulds), however, indicate the important role of algae in phosphogenesis in that they represent favourable sites for apatite growth, a result confirmed by the high relative concentration of  $\text{P}_2\text{O}_5$  in their frustules as shown by EDX analysis.

The diatom assemblages indicate restricted marine conditions. The silica released from the dissolution of diatoms primarily participates in chert, Porcellanite and/or glauconite formation.

In brief, the source of phosphorus could be subdivided into

- (1) Extrabasinal sources due to the weathering of the hinterland and
- (2) Intrabasinal sources including upwelling and organic sources due to the dissolution of diatoms.

A marked variation in francolite chemistry is noticed.  $\text{FeO}$ ,  $\text{MgO}$  and  $\text{Na}_2\text{O}$  are relatively higher in the francolites of the phosphorite-bearing siliciclastics.  $\text{CaO}$  and  $\text{F}$  are, in contrast, rich in those of the phosphorite-bearing carbonates. Such variation may result from the impact of facies control. Moreover, a remarkable variation in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{CaO}$ ,  $\text{P}_2\text{O}_5$  and  $\text{MgO}$  content in the analyzed francolites from the same phosphate horizon is found, a finding which may be due to the effect of weathering, reworking and grain size and abundance of micro-organisms of the phosphorite particles.

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