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## Geology and Geochemistry of the Phosphorite Deposits, Sibaiya Area, Nile Valley, Egypt

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### ABSTRACT

The present work aims to study the phosphorite deposits of the Late Cretaceous age that are belonging to the Duwi Formation. It is well exposed in Sibaiya area as oxidized phosphorite with yellowish to brown colour and non-oxidized phosphorite in some parts with grey to black color. This Formation could be classified into lower phosphorite, middle shale and upper phosphorite members. The lower phosphorite member is the most economic one. The average thickness of this member is 3.3 m in the western part, while it reaches 4.8 m in the eastern part of Sibaiya area. The phosphate beds are composed of peloids, Bioclasts of bone and teeth fragments and Coprolites. A geochemical analysis were done for, CaO, P<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO in% in addition to heavy metals Cd, Cr, Cu, Ni, Sr, Zn in ppm as well as U, Th and Ra in ppm. The results show that the average of P<sub>2</sub>O<sub>5</sub> and U contents in oxidized phosphorite are 24.18 % and 69 ppm respectively. Meanwhile in non-oxidized phosphorite, they are 27.8 % and 85 ppm respectively. The variation in P<sub>2</sub>O<sub>5</sub> and U contents in Sibaiya phosphorite rocks are probably related to depositional and diagenetic aspects. Generally, the Sibaiya phosphorite could provide an economic value for production of phosphoric acid and extracted of U as by-product.

### 1. INTRODUCTION

The phosphorite rock is considered as one of the important ore deposits either in Egypt or over the world. It is the main raw material for phosphatic fertilizers and phosphoric acid industries. Phosphorite deposits in Egypt are confined to the Duwi Formation belonging to the Campanian- Maastrichtian age. These deposits form discontinuous extended belt from Safaga - El Qusseir region on the Red Sea coast through the Sibaiya district to the (Kharga - Dakhla) Oases region in the Western Desert. The Phosphorite (Duwi) Formation is overlain by Dakhla Formation and assigned as Upper Campanian to Early Maastrichtian age [1,2,3].

The Sibaiya area is located between Idfu and Esna, central Eastern Desert, Egypt. The western Sibaiya area is bounded by longitudes 32° 39' and 32° 46' E and latitudes 25° 04' and 25° 11' N, whereas, the eastern Sibaiya area is bounded by longitudes 32° 49' - 33° 03' E and latitudes 25° 06' - 25° 12' N (Fig. 1).

In general, the litho-stratigraphic section of Sibaiya area is based by Qusseir shale formation of the Nubia group, overlain by the Duwi Formation and Dakhla Formation at the top. The Duwi Formation comprises three members; the lower one is the productive phosphorite beds. Zidan [4] reported that the Duwi Formation is un-conformably overlying the Qusseir shale member with an undulating surface.

The Nuclear Material Authority report[5] concluded that the phosphorite reserves in Egypt are not clearly indicated but the estimated as geological reserves point to about 50 million tons at Red Sea Coast, 70 million tons at Sibaiya (Nile Valley) and 7000 million tons at Abu Tartur area. According to World Codes, the level of accuracy in calculating geological reserves is very low and the mineral risk ratio is over 50% [6].

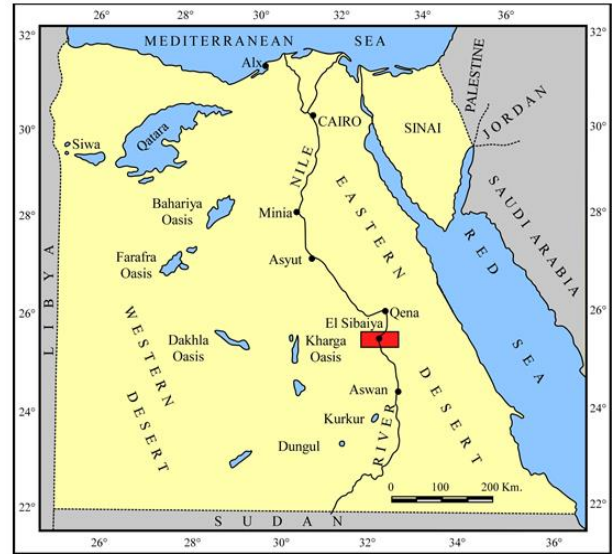
Petrographic studies indicate that phosphate beds consist of phosphatic particles (Peloid grains, Bioclasts and Coprolites) and non-phosphatic particles that are

represented by dolomite, Calcite, hematite, Pyrite, gypsum, strontianite and detrital quartz as matrix and cement material [7,8].

The geochemistry of phosphorites and its main mineral constituent, francolite, have been widely studied due to their economic importance [9] and the potential utility of their geochemistry to reveal its paleo-marine chemistry [10]. Variability in the chemical composition of francolite may reflect a difference in original composition and modification during diagenesis [9]. All sedimentary phosphorites, all over the world, are mainly composed of carbonate fluorapatite (traditionally known as francolite), but the fluorine content increases with age. The francolite of the Upper Cretaceous-Lower Tertiary age contains 3 to 5 % F, with F/P<sub>2</sub>O<sub>5</sub> ratio of about 0.11 [11].

Zidan [12] reported that the Egyptian phosphorite rocks were deposited in reducing environment with grey to black color. The change to yellowish brown color occurred due to oxidizing conditions by geochemical weathering. The F<sub>2</sub>O<sub>3</sub> liberated from pyrite formed hematite, while the SO<sub>3</sub> combined with CaO forming anhydrite. Marine phosphorites are considered a good source of uranium where, they contain a U value between 50-200 ppm, which represents 15 to 60 times greater than that of crustal abundances [13]. Averages of the uranium content in the Egyptian phosphorites were estimated as 85, 68 and 24 ppm for Sibaiya, Red Sea and Abu-Tartur phosphate deposits respectively [14]. Zidan (op.cit) pointed out that the average U content in the phosphatic fertilizers (SSP) is 72 ppm that represents a highly probable pollution source for agricultural soil hence, for water and plants. Some plants absorb much more U than others, which may reach up to 100 ppm, while the normal absorbed uranium by plants usually ranged from 0.2 to 1 ppm [15]. Abu Tartur phosphorite contains the highest content of REEs up to 2000 ppm relative to Sibaiya phosphorite of about 150 ppm [16]. The total of REEs content in present phosphorite of Sibaiya area, Nile valley is 228.3 ppm lower than Abu Tartur phosphorite, 1718 ppm [8].

The principal aim of the present study concerns geological and geochemical characterization of oxidized and non-oxidized phosphorite rocks in Sibaiya area in both sides of the Nile Valley. Therefore, litho-stratigraphic and geochemical studies of the investigations phosphorite rocks at this area were carried out.



**Fig. (1): Key map showing the location of the studied area**

## 2. MATERIAL AND METHODS

Twenty-one representative phosphorite samples were collected from 6 litho-stratigraphic sections of Sibaiya area to cover the lower phosphorite member of the Duwi Formation. These samples were prepared and subjected to complete wet chemical methods analysis to estimate the contents of major oxides. Meanwhile, the trace elements were measured using Philips X-ray fluorescence spectrometer (XRF). The uranium content was determined radiometrically using a gamma-ray spectrometer and chemically by spectro-photometric technique using arsenazo III as indicator. The REEs content was determined by using Induced Couple plasma (ICP).

## 3. Geologic Setting

The Duwi Formation in the studied area is classified after Issawi et al. [2,3] and Zidan [12] into Lower phosphorite, Middle shale and Upper phosphorite members. In the present study, the exposed phosphorite beds of the Duwi Formation are unconformably overlies the Campanian Qusseir shale member with an undulating erosion contact, and are conformably overlain by the marine laminated Maestrichtian grey to black shale and marls of the Dakhla Formation (Figs. 2,3,4 and 6). The Duwi Formation in Sibaiya area is composed of oxidized phosphorite with yellowish to brown colour, coarse to fine grains, moderately hard and non-oxidized phosphorite in some parts with grey colour. Generally, Sibaiya phosphorites are intercalated with thin black shale, dolomitic lenses and oyster phosphatic limestone beds (Figs. 2, 3). The Duwi Formation in west Sibaiya

area vary in thickness from 11.35 to 11.5 m attaining its maximum thickness (11.5 m) in the southern part of the area. While the thickness in east Sibaiya area ranges from 9 to 10.8 m attaining its maximum thickness (10.8 m) in central part of the area (Figs. 2,3,4 and 6).

### 3.1. Lower phosphorite member

This member consists of a moderately hard oxidized phosphorite with yellowish to brown colour (Figs. 4 and 5) and non-oxidized phosphorite in some parts with grey colour (Figs. 6 and 7). The phosphorite beds of Sibaiya area are intercalated with black shale, dolomitic and chert lenses as well as oyster phosphatic limestone beds. The total thickness of this member in west Sibaiya area ranges from 3.1 m to 3.4 m with an average of 3.3 m attaining its maximum thickness (3.4 m) in the southern part of the area (Figs. 2, 6, 7). While in east Sibaiya area, it ranges from 4 to 6 m with an average of 4.8 m attaining its maximum thickness (6 m) in southern part of this area (Figs. 3, 4, 5). The Lower phosphorite member is considered as the economic productive phosphorite beds in Sibaiya area (Figs. 2 - 7).

### 3.2. Middle shale member

This member is mainly composed of glauconitic shale, siltstone and grey shale characterized by the presence of gypsum veinlets and ferruginous staining. This member has thickness ranges from 8 to 9 m with an average of 8.3 m, attains its maximum thickness (9 m) in the central part of the west Sibaiya area (Figs. 2, 6). Meanwhile in east Sibaiya area, it ranges from 4 to 6 m with an average of 5 m, attaining its maximum thickness (6 m) in central part of the studied area (Figs. 3, 4)

### 3.3. Upper phosphorite member

This member is composed of hard oxidized dolomitic phosphorite beds with yellowish to brown colour, intercalated with grey to black shale lenses. Its thickness varies from 10 to 25 m with an average of 20 m (Figs. 2,3,4 and 6).

### 3.4. Dakhla Formation

In the studied area the Dakhla Formation is composed of grey to black shale intercalated with silt clay and marl beds. The thickness of the Dakhla Formation in west Sibaiya area ranges from 4 to 15 m with an average of 9 m, and it attains its maximum thickness in the northern part of the area about 15 m (Figs. 2, 6). While in east Sibaiya area, it ranges from 8 to 18 meters thick with an average of 13.3 m, and it attains its maximum thickness in northern part of the area about 18 m (Figs. 3,4).

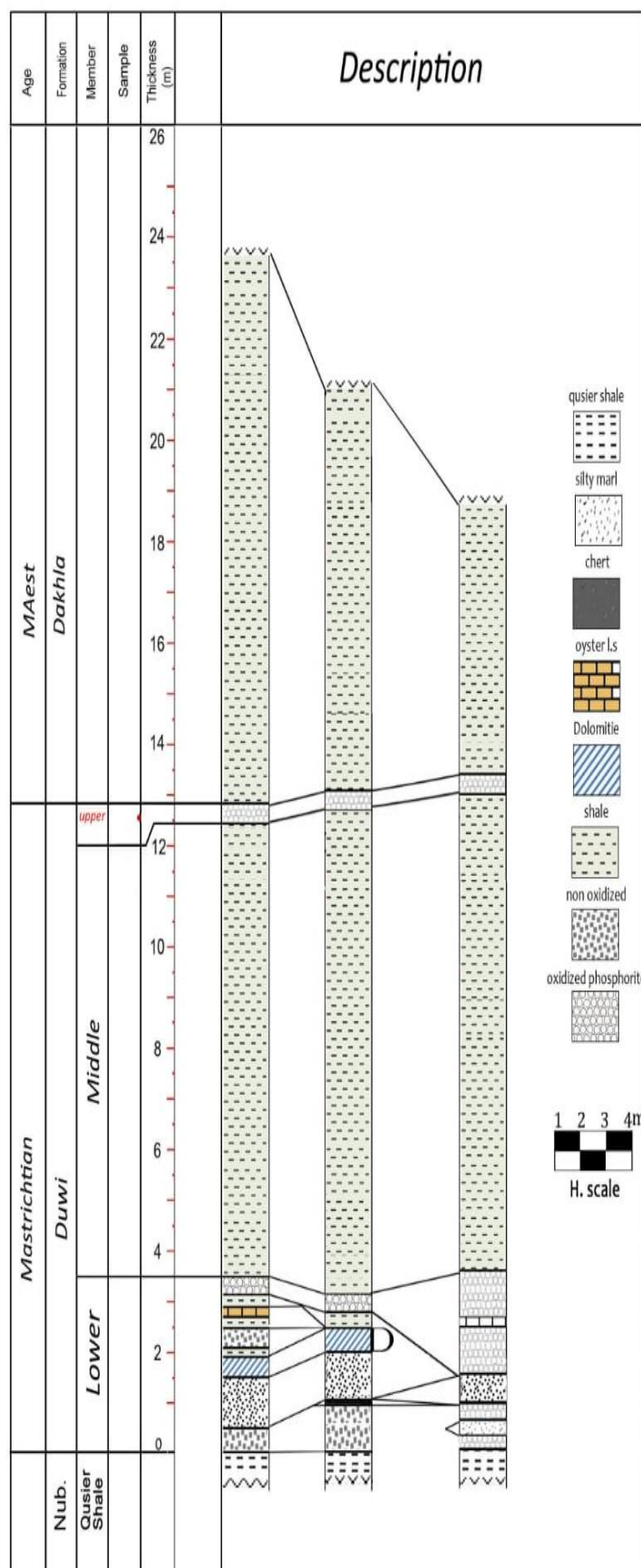


Fig. (2): Litho-stratigraphic of the studied sections (1,2 and 3) in west Sibaiya area, Nile Valley, Egypt



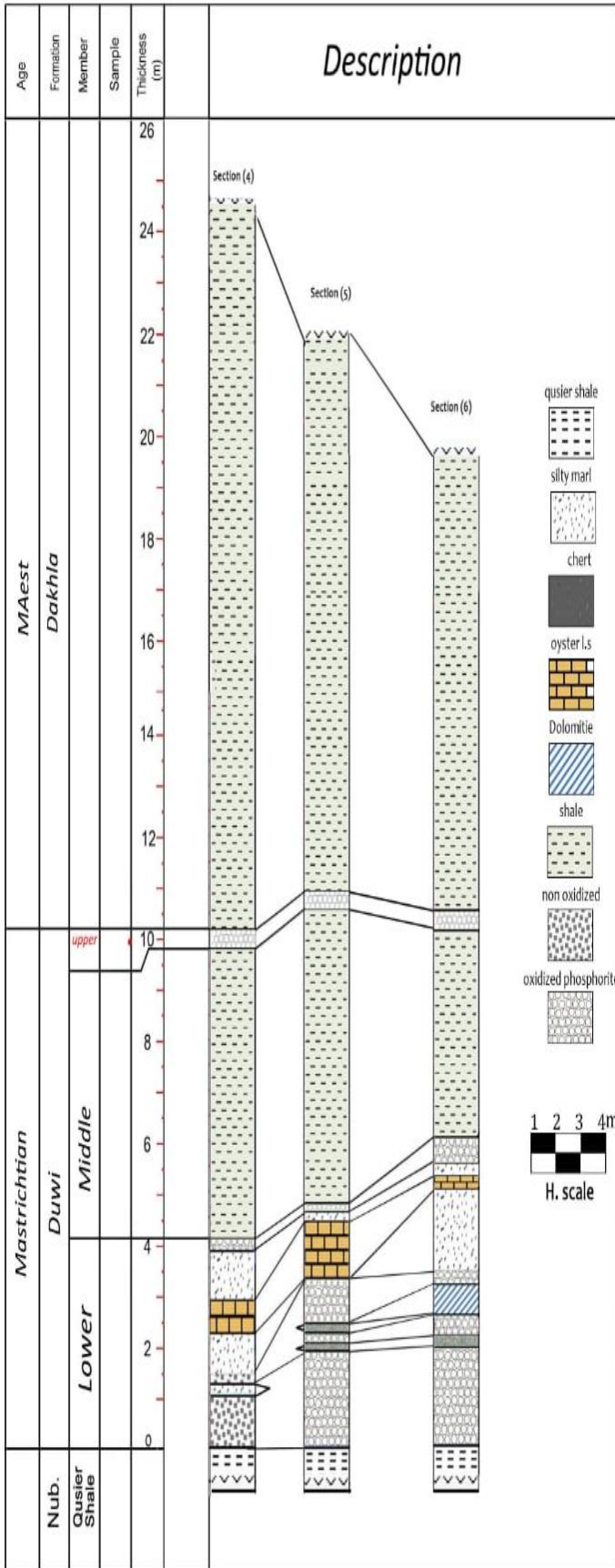


Fig. (3): Litho-stratigraphic of the studied sections (4, 5 and 6) in east Sibaiya area, Nile Valley, Egypt

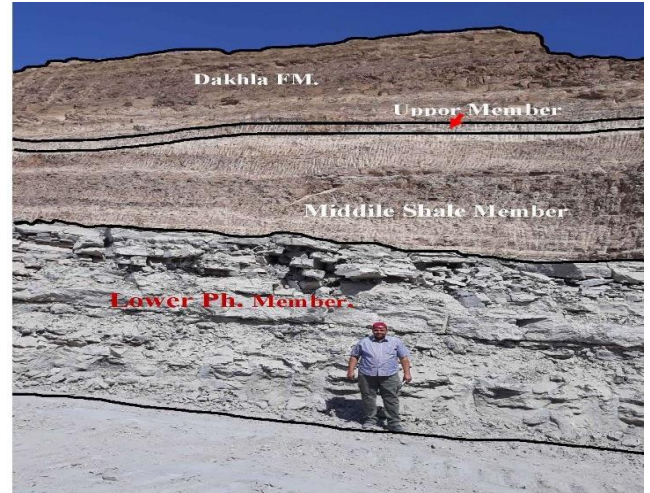


Fig. (4): Photograph showing the Duwi and Dakhala Formations, east Sibaiya area, Nile Valley, Egypt



Fig. (5): Photograph showing Lower phosphorite member of the Duwi Formation, east Sibaiya area, Nile Valley, Egypt

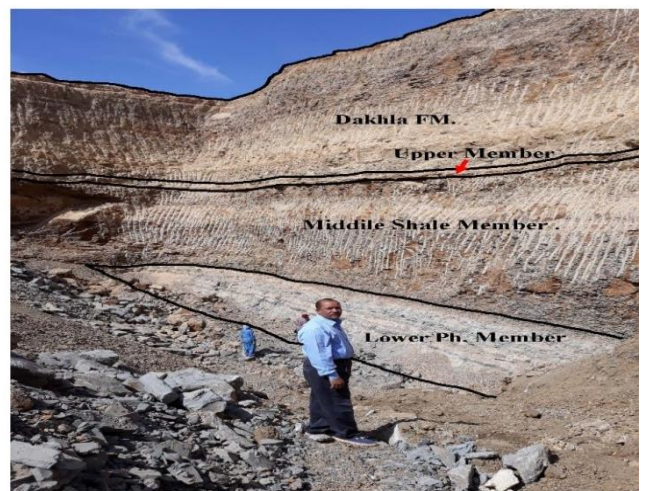


Fig. (6): Photograph showing the Duwi and Dakhala Formations, west Sibaiya area, Nile Valley, Egypt



**Fig. (7): Photograph showing Lower phosphorite member of the Duwi Formation, west Sibaiya area, Nile Valley, Egypt**

#### 4. Petrographic Features

Kolkila et al [17,7,18]; classified the phosphorite on the basis of the constituents into phosphatic particles and non-phosphate particles.

In Sibaiya area, three main varieties of phosphatic particles are present as follows:

- a) Peloid grains.
- b) Bioclasts.
- c) Coprolites.

These three types of phosphatic particles are allo-chemical component modified from the crystalline phosphorite mineral (collophane). The phosphate of the marine phosphorites of Sibaiya area Nile Valley occurs as a cryptocrystalline or amorphous material (collophane) that varies in colour from brownish yellow to black, and it normally consists of peloids (pellets), bioclasts nodules, bone fragments and coprolites.

Tucker[19] pointed out that the amorphous grains are peloids formed by algal micritization of skeletal material.

The term "peloid" might seem to be appropriate for such deposits because it is an umbrella term allowing description without implication of specific genesis [20]. Moreover, the main lines of the petrogenic classification are demonstrated by Riggs [21]. which were also used by Schoter[22] in his study on the Egyptian phosphorites.

Texturally, the peloids process different shapes and sizes. They may be spherical or ovoid, irregularly or lath-shaped, Ovoid-shaped grains resemble phosphatized fecal pellets. Most peloids are well-rounded to sub-rounded and are of faecal origin.

Much of the phosphorites consist of pellets up to several millimeters in diameter and composed of colophane embedded in a matrix of apatite with smaller pellets. In the studied thin sections, pellets of apatite grains are embedded in carbonate and silica cement (Figs. 8a, 8b).

In the present thin sections, bioclastic phosphorite consisting of bone and teeth fragments as well as angular to subrounded pellets of apatite grains are embedded in carbonate and silica cement (Figs. 8c, 8f).

Coprolites are believed to be pulses of excrements that had passed through diagenesis. They commonly reach 2.0 mm in diameter with irregular shape and convoluted surfaces. The coprolites were recorded in some thin sections. They are elongated, with apatite pellets, embedded in carbonate cement as shown in (Figs. 8d, 8e).

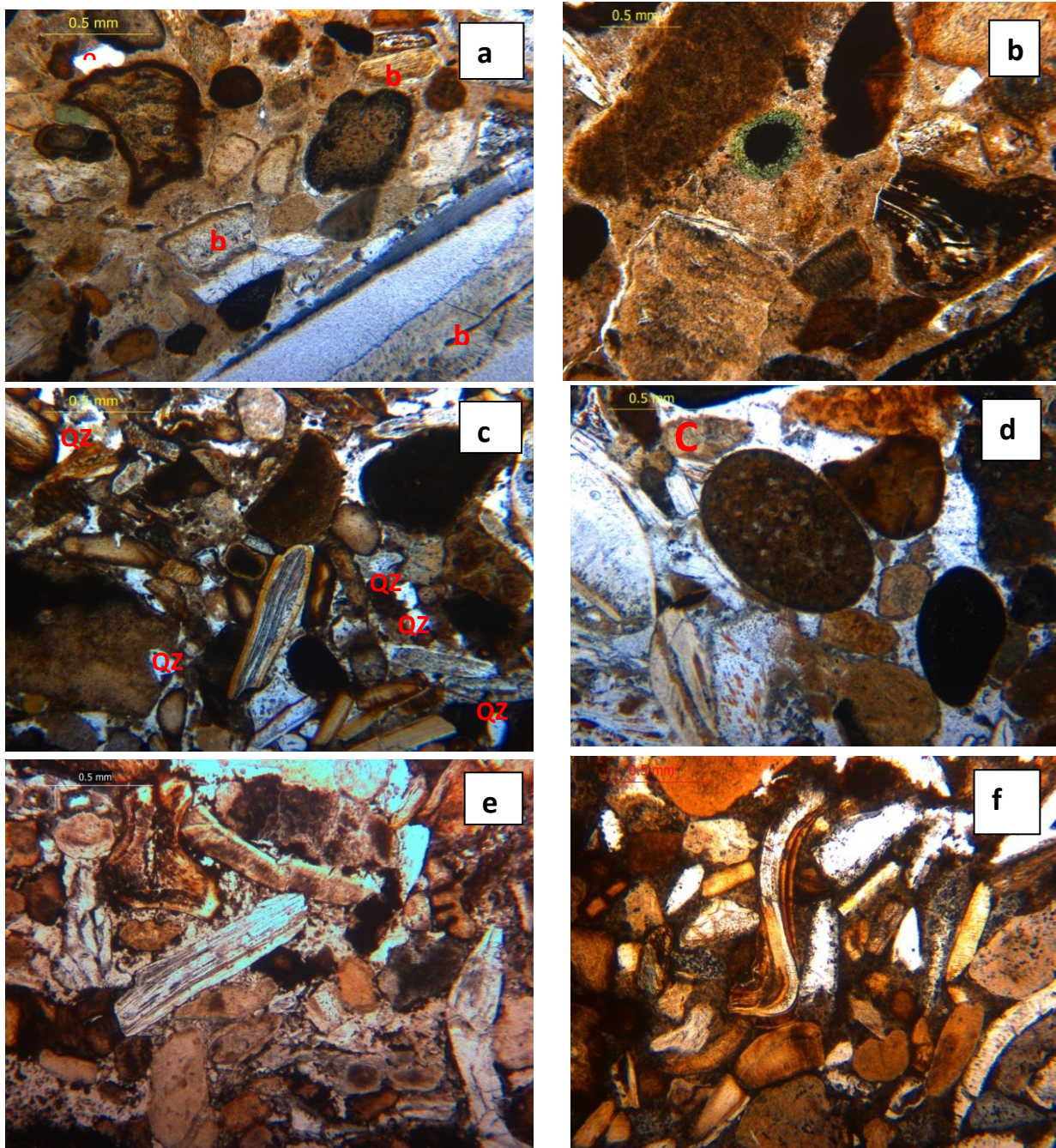
In the studied samples, the non-phosphatic materials are represented by dolomite, calcite, hematite, pyrite, gypsum, strontian and detrital quartz as matrix and cement materials. This indicates that the Sibaiya phosphorites were deposited under shallow marine conditions near the shore (Figs. 8a-8c and 8d, 8e, 8f).

Quartz representing the most common form of silica occurs both as detrital grains and detrital quartz are usually present as angular to sub-angular grains, and sometimes as rounded to sub-rounded in the silt to medium sand size grades.

Glaucinite is uncommonly present in some samples. The majority of glaucinite grains are generally well-rounded in the medium "sand size" range. Otherwise, they are sub-rounded to sub-angular. Phosphatic and glaucinitic facies are often found together in marine various ages.

The presence of glaucinite grains within the non-oxidized phosphorite (grey to black in colour) as shown in (Figs. 8b), reflects reducing environment of deposition[19].





**Fig (8): Photographs showing different constitutes of the studied phosphorites:**

Photomicrograph showing sub-angular to sub-rounded oxidized apatite grains, brown colour. Note: internal structure of bone (b) and glauconite grain with (green colour) (g) and detrital quartz grain (Qz) embedded in carbonate cement, P.PL. b) Photomicrograph showing elongated oxidized apatite grains, yellowish to, brown colour and bone fragments. Note: non-oxidized apatite grain black colour coated by glauconite with green colour embedded in carbonate cement P.PL. c) Photomicrograph showing bioclastic phosphorite consisting of oxidized and non-oxidized apatite grains, brown and black colours as well as bone and teeth fragments beside some detrital quartz grains (Qz) embedded in carbonate cement and silica cement. P.PL. d) Photomicrograph showing yellowish to brown colour oxidized apatite grains and some grains of non-oxidized apatite with black colour. Note: coprolite grain (c) embedded in carbonate cement P.PL. e) Photomicrograph showing bioclastic phosphorite consisting of oxidized apatite grains sub-rounded, yellowish colour as well as bone fragments elongated. Note: elongated coprolite grain (c) embedded in carbonate cement P.PL. f) Photomicrograph showing bioclastic phosphorite consisting of oxidized apatite grains, sub-rounded, to well-rounded yellowish to brown colour as well as bone and teeth fragments embedded in silica cement. P. Pl.

## 5. RESULTS AND DISCUSSION

### 5.1 Geochemical Characterization

Geochemically, the elemental composition of the phosphorite rock is usually grouped into two essential groups of major elements; the first is predominantly located within the apatite lattice and includes CaO, P<sub>2</sub>O<sub>5</sub>, F, CO<sub>2</sub> and Na<sub>2</sub>O while the second group locates outside the apatite crystal lattice and includes SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O<sup>(23)</sup>. Other components Fe<sub>2</sub>O<sub>3</sub>, MgO and MnO are usually introduced to the phosphorite deposits by weathering process. Generally, the trace elements in phosphorites may be associated with detrital minerals, organic matter, introduced by weathering and these located within the apatite lattice.

Twenty-one representative phosphorite samples (15 oxidized phosphorite and 6 non - oxidized phosphorite) of Sibaiya area, were subjected to chemical analysis to determine the major, trace, RREs and radioactive elements contents (Tables 1-4).

#### 5.1.1. Major oxides composition

The chemical analysis shows that the Sibaiya phosphorite deposits are dominated by CaO content in the oxidized phosphorite of the Duwi Formation ranging between 30 and 42 % with an average of 36.54 % (Table 1). In non-oxidized phosphorite, it varies from 39 to 42.25 % with an average 40.25 (Table 2). The P<sub>2</sub>O<sub>5</sub> content in the oxidized phosphorite ranges from 19.2 to 29 with an average of 24.18, while in the non-oxidized phosphorite it ranges from 26 to 29.2 with an average 27.8. The MgO content in the oxidized phosphorite ranges from 2.5 – 9.5 % with an average of 5.9 %, while in non-oxidized phosphorite it ranges from 2.6 – 6.2 % with an average 3.6. The Fe<sub>2</sub>O<sub>3</sub> content in oxidized phosphorite ranges from 3 to 5.5 with an average of 4.8, while in non-oxidized phosphorite it ranges from 2.4 to 3.1 with an average 2.91. The averages of Al<sub>2</sub>O<sub>3</sub>, F, Na<sub>2</sub>O and K<sub>2</sub>O contents were also calculated (Tables 1, 2).

Usually, the CaO and P<sub>2</sub>O<sub>5</sub> are the main components of apatite minerals while MgO content is related to presence of dolomite mineral. The observed variation in the average content of P<sub>2</sub>O<sub>5</sub> between oxidized phosphorite (24.18 %) and non- oxidized phosphorite

(27.78 %) of Sibaiya area may reflect the diagenetic processes which cause limited replacement of P<sub>2</sub>O<sub>5</sub> by other components such as SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc. which led to reduces the grade of the phosphorite.

The variation in the average content of Fe<sub>2</sub>O<sub>3</sub> between oxidized phosphorite (4.8 %) and non- oxidized phosphorite (2.91 %) may be reflecting the digenetic process. Zidan [12] suggested that the Egyptian phosphorite rocks were deposited in a reducing environment with grey to black colour. The change to yellowish brown colour occurred oxidizing chemical by weathering. The Fe<sub>2</sub>O<sub>3</sub> liberated from pyrite formed hematite while the SO<sub>3</sub> combined with CaO forming anhydrite.

Generally, the P<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub> and MgO % contents are widely used for quality evaluation in industry. Zidan[7] classified the phosphorite ore into; high grade with P<sub>2</sub>O<sub>5</sub> content more than 27%, medium grade has P<sub>2</sub>O<sub>5</sub> ranging from 23 – 27% and low grade with P<sub>2</sub>O<sub>5</sub> less than 23%. According to that classification, the studied phosphorites of Sibaiya area considered as medium grade for oxidized phosphorite (average of 24.18 % P<sub>2</sub>O<sub>5</sub>) and high grade for non- oxidized phosphorite (average of 27.78% P<sub>2</sub>O<sub>5</sub>).

The average contents of major oxides of Sibaiya phosphorite, compared to some published data in Egypt are shown in Table (3). The result showed that the P<sub>2</sub>O<sub>5</sub> content in the non-oxidized phosphorite of Sibaiya area (27.78 %) is higher than the oxidized phosphorite (24.18 %), Abu Tartur phosphorite (25.7 %) and Mahamid phosphorite (26.4 %), while it is lower than the Red Sea phosphorite (28.3 %). On the other hand, the Fe<sub>2</sub>O<sub>3</sub> content in non-oxidized phosphorite (2.91 %) is lower than the oxidized phosphorite (4.80%), in Abu Tartur phosphorite (4.2 %) and in Mahamid phosphorite (3.9 %) while it higher than in Red Sea phosphorite (1.6 %). Also, the MgO content in the non-oxidized phosphorite (3.6 %) is lower than in the oxidized phosphorite (5.9 %), Abu Tartur phosphorite (4.8 %) and Mahamid phosphorite (4.4 %) and Red Sea phosphorite (4.3 %) as shown in Table (3). These may reflect a different depositional environment which causes this character of the phosphorite constitutes.

**Table (1): Chemical analysis of the major oxides (wt%) of the oxidized phosphorite of Duwi Formation, Sibaiya area, Nile Valley, Egypt**

NO.	S.NO.	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	F	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	TiO <sub>2</sub>	L.O.I
1	4	21.8	35.3	7.6	11	5	1.7	1.8	1.5	0.2	0.04	0.08	13
2	11	24.1	35	5.4	13	5	2.2	1.8	1.2	0.1	0.02	0.05	10
2	12	24	36	5.5	13.5	5.5	2.4	2	1.6	0.2	0.03	0.02	9.6
2	14	22.7	35.3	6.9	10.6	4.8	1.8	1.9	1.5	0.2	0.04	0.02	14
2	15	20.0	31.2	9.5	11.0	5.3	1.4	2.5	1.1	0.2	0.03	0.03	14
3	19	24	37.5	5.8	11.5	4.5	1.0	1.9	1.2	0.1	0.02	0.03	10
3	21	24	38	4.7	11	5	1	1.2	1	0.1	0.03	0.03	13
3	22	25	39	7	10.9	4.9	1.5	2	1.1	0.3	0.02	0.02	8.91
5	32	29	42	2.8	7.5	5.5	2	1.5	1	0.4	0.03	0.02	8
5	33	29	38	4.7	11	3	2.1	1.5	1.2	0.1	0.02	0.03	11
5	34	25.6	37.3	3.7	11.5	5.2	2.3	1.9	1.3	0.2	0.05	0.02	10
6	38	26	39	5.3	9.2	4.8	1.9	2	1.1	0.2	0.03	0.02	9.7
6	39	19.2	30	9.3	13	5.1	1.1	2.6	1.5	0.4	0.02	0.03	16
6	40	26.8	40	3.5	11	3.3	1.7	1.5	1.2	0.2	0.02	0.02	10.8
6	43	21.5	33.6	7.5	13.5	5.2	1	1.8	1.6	0.2	0.03	0.03	13.7
Min.		19.2	30	3.5	9.2	3	1	1.2	1	0.1	0.02	0.02	8.91
Max.		29	42	9.5	13.5	5.5	2.4	2.6	1.6	0.4	0.05	0.08	14
Ave.		24.2	36.5	5.9	9.74	4.80	1.7	1.86	1.27	0.20	0.02	0.03	11.44

**Table (2): Chemical analysis of the major oxides (wt%) of the non-oxidized phosphorite of Duwi Formation, Sibaiya area, Nile Valley, Egypt**

No.	S.No.	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	F	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	TiO <sub>2</sub>	L.O.I
1	1	27	39	3.3	12	3.1	2.3	1.4	1	0.2	0.2	0.03	9
1	2	26	39	6.2	10.1	2.4	1.3	1.7	1.1	0.2	0.03	0.03	12
1	5	28	41	4	10	3	1.5	1.2	1.2	0.2	0.02	0.04	10
1	6	29.2	42.5	2.6	9	3	3	1.4	1.2	0.1	0.01	0.02	8
4	26	27.5	40	2.8	9.2	3	2.5	1.6	1.2	0.2	0.08	0.02	11
4	27	29	40	2.7	9	3	2.4	1.6	1.1	0.2	0.02	0.02	11
Min.		26	39	2.6	9	2.4	1.3	1.2	1	0.1	0.01	0.02	8
Max.		29.2	42.5	6.2	12	3.1	2.5	1.7	1.2	0.2	0.08	0.04	12
Ave.		27.8	40.3	3.6	9.88	2.91	2.2	1.48	1.13	0.18	0.03	0.02	10.2



**Table (3): Correlations between average contents of major oxides (wt%) of Sibaiya phosphorite, Nile Valley compared to some published data in Egypt**

Locality Oxide (%)	Oxidized Sibaiya phosphorite	Non-oxidized Sibaiya phosphorite	Abu Tartur phosphorite[24]	Mahamid phosphorite [8]	Red Sea phosphorite [25]
P <sub>2</sub> O <sub>5</sub>	24.18	27.78	25.7	26.4	28.3
CaO	36.54	40.25	38.8	38.4	38.4
Fe <sub>2</sub> O <sub>3</sub>	4.80	2.91	4.2	3.9	1.6
MgO	5.9	3.6	4.8	4.4	4.3
SiO <sub>2</sub>	9.74	9.88	11	11.6	8.9
Al <sub>2</sub> O <sub>3</sub>	1.86	1.48	1.8	1.8	1.6
F	1.67	2.16	1.7	2	2.9
Na <sub>2</sub> O	1.27	1.13	1.1	1.2	1.2
K <sub>2</sub> O	0.2	0.18	0.2	0.2	1

### 5.1.2. Trace Elements Distribution

The abundance and distribution of the trace elements in the phosphorite samples of the Duwi Formation at Sibaiya area are given in Tables 4 and 5. The results showed that the studied phosphorite deposits are enriched in Sr, Cr, Cu Ni and Zn relative to low contents of Cd and Pb. The Sr in oxidized phosphorite of the Duwi Formation varies from 413 ppm to 754 ppm with an average of 555 ppm, whereas in the non-oxidized phosphorite it ranges between 603 ppm and 745 ppm with an average of 685 ppm. Gill [26] reported that Sr and Ba are associated with francolite mineral. Zidan[4] concluded that presence of Sr in the phosphorite is related to presence of strontianite mineral within phosphorite deposits.

The Zn content in oxidized phosphorite ranges from 13 ppm to 181 ppm with an average of 120 ppm, while in the non-oxidized phosphorite it ranges from 27 ppm to 168 ppm with an average of 122 ppm (Tables 4 and 5). Altschuler [27] concluded that the very high content of Zn is attributed to the sulphate

phase admixed in phosphorites. He also stated that enrichment in phosphorites reflects their substitution for Ca in apatite.

The Cu in oxidized phosphorite oscillates from 11 ppm to 33 ppm with an average of 23 ppm, while in the non-oxidized phosphorite, it ranges between 11 ppm and 29 ppm with an average of 20 ppm (Tables 4 and 5). Basta and El Kammar[28] concluded that Cu and Ni are most probably concentrated within carbonaceous matter. The fact that the skeletal apatite is highly enriched in carbonaceous matter compared to the bulk phosphorites explains the extensive depletion of weathered apatite in the heavy metal [29].

It is noted that there is a relative similarity between the contents of Cd, Cr, Cu, Ni, Pb and REEs in the studied phosphorite and other Egyptian phosphorites, except the REEs content in AbuTarturphosphorite (1987 ppm) are very higher than the studied and other Egyptian phosphorites as given in (Table 6).

**Table (4): Concentrations of trace elements (ppm) of oxidized phosphorite of the Duwi Formation, Sibaiya area, Nile Valley, Egypt**

Sec. No.	S.NO.	Cd	Cr	Cu	Ni	Zn	Pb	Sr
1	4	7	99	27	41	153	2	450
2	11	8	155	26	42	158	4	561
2	12	8	97	26	43	155	1	556
2	14	6	97	26	43	155	1	457
2	15	8	31	11	21	74	1	413
3	19	10	113	33	41	72	3	583
3	21	6	30	11	20	72	1	499
3	22	11	115	28	45	205	4	587
5	32	21	155	31	48	97	2	754
5	33	6	143	27	44	13	3	751
5	34	17	85	20	41	95	7	601
6	38	10	160	31	46	144	5	622
6	39	7	30	11	21	75	1	421
6	40	13	158	19	44	181	8	628
6	43	8	152	24	41	157	4	435
Min.		4	30	11	20	13	1	413
Max.		21	160	33	48	181	8	754
Ave.		9	108	23	39	120	3	555

**Table (5): Concentration of some trace elements (ppm) of non-oxidized phosphorite of the Duwi Formation, Sibaiya area, Nile Valley, Egypt**

Sec.No.	S.NO.	Cd	Cr	Cu	Ni	Zn	Pb	Sr
1	1	4	135	11	12	168	2	654
1	2	10	89	29	41	157	9	603
1	5	17	125	11	12	130	11	714
1	6	7	138	24	26	27	5	733
4	26	10	89	29	41	157	9	663
4	27	12	139	14	30	95	2	745
1	1	4	135	11	12	168	2	654
Min.		4	89	11	12	27	2	603
Max.		17	139	29	41	168	11	745
Ave.		10	119	20	27	122	6	685

**Table (6): Average of trace elements content and REEs(ppm) of Sibaiya Phosphorite, Nile Valley compared to some published data in Egypt**

Oxide (%)	Oxidized Sibaiya phosphorite	Non-oxidized Sibaiya phosphorite	Abu Tartur phosphorite [24]	West Sibaiya phosphorite [12]	Red Sea phosphorite [14]
Cd	10	9	11	3	10
Cr	119	108	116	117	115
Cu	20	23	24	23	17
Ni	27	39	36	38	34
Zn	122	120	140	73	200
Pb	6	3	5	4.5	-
REEs	234.2	222.4	1987	150	160

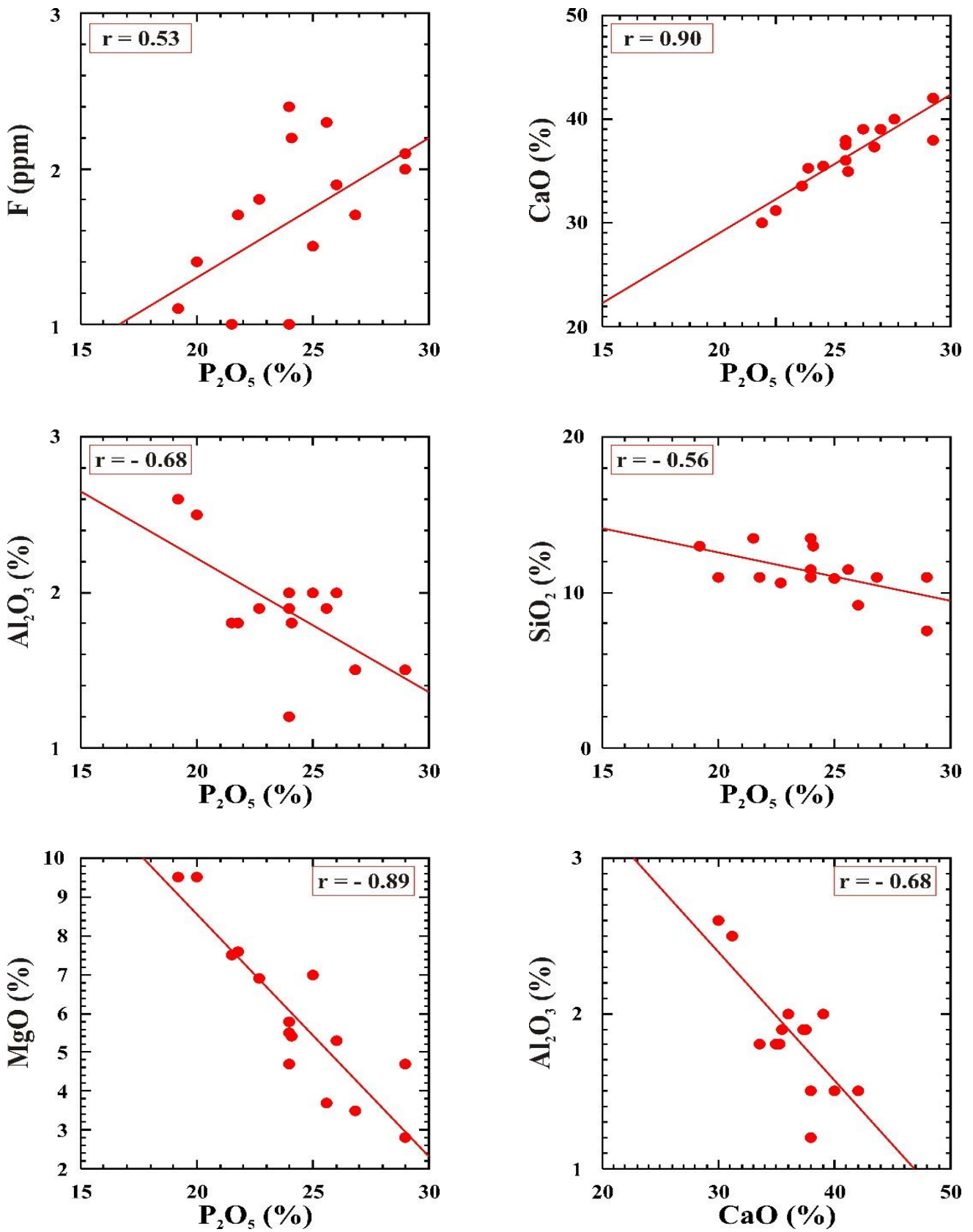
## 5.2. Inter-relationships of elements

The statistical treatment of analytical data of the Sibaiya phosphorites shows a positive correlation between  $P_2O_5$  and other elements that are located inside the apatite lattice such as CaO, F and Sr as expected. At the same time,  $P_2O_5$  shows a negative correlation with other elements that located outside the apatite lattice such as  $Al_2O_3$ ,  $SiO_2$  and MgO. Generally, there are strong positive correlations between  $P_2O_5$  and CaO, F and Sr ( $r = 0.90$ ,  $r = 0.70$  and  $r = 0.97$  respectively). Also the strong positive correlation between CaO and Sr ( $r = 0.83$ ) as shown in (Figs. 9 and 10), may indicate that a high substitution between these elements occurs in the apatite structure. Dabous [30] attributed the strong positive correlation between  $P_2O_5$  and CaO in the Nile Valley phosphorites to the presence of calcite mineral as a cementing

material. On the other hand, there is a negative correlation between  $P_2O_5$  and  $Al_2O_3$ ,  $SiO_2$  and MgO ( $r = -0.68$ ,  $-0.56$  and  $-0.89$  respectively). Also a negative correlation between CaO and  $Al_2O_3$  for Sibaiya phosphorites is detected ( $r = -0.68$ ) as shown in (Fig. 9). These reflect that elements are located outside the apatite lattice. Zidan [12] suggested that the  $Al_2O_3$ ,  $SiO_2$  and MgO are related to the clay cement.

The  $P_2O_5$  shows positive correlations with Ni and Cu ( $r = 0.52$  and  $0.65$  respectively) in Sibaiya phosphorites (Fig. 10). The enrichment of some trace elements in phosphorites may be due to the reduction conditions induced by organic matter [31]. The presence of trace elements in the Nile Valley phosphorite is associated with detrital minerals [10].





**Fig. (9):** Correlation between major oxides (wt%) and trace elements (ppm), Sibaiya phosphorite, Nile Valley, Egypt

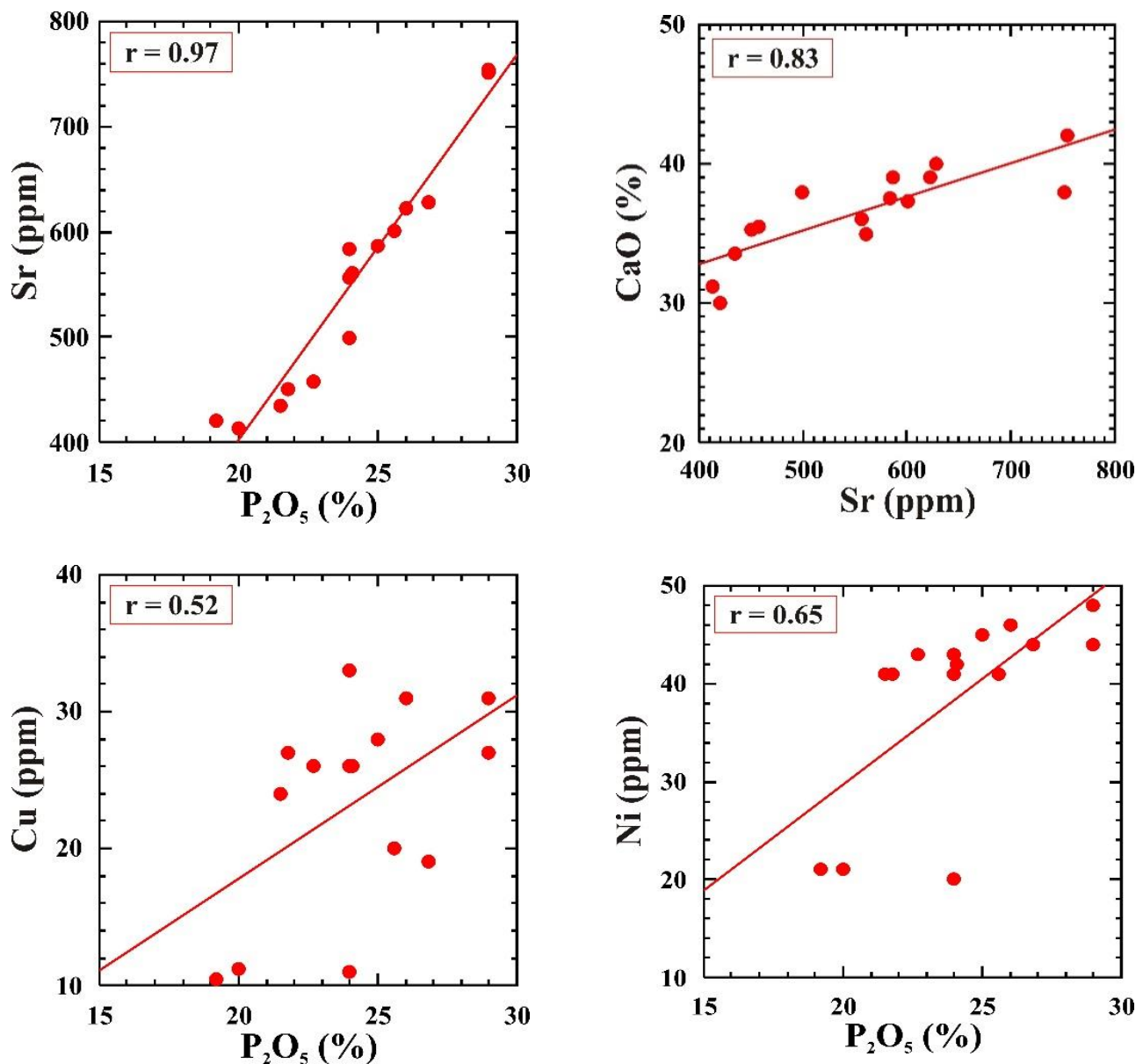


Fig.(10): Correlation between major oxides(wt%) and trace(ppm) elements, Sibaiya phosphorite, Nile Valley, Egypt

### 5.3 Rare Earth elements (REEs) contents of Sibaiya phosphorite

The discovery of REEs in Egyptian phosphorite can be dated back to the year 1888, when Zittel reported these rocks in Qift, near Qena. The geochemistry and economic importance of REEs in the Western Desert phosphorite have first been

considered by El-Kammar[32] who reported REEs abnormality in Abu Tarturphosphorite. Amin and Zidan[16] stated that the average REEs content in Abu Tarturphosphorite is 1718ppm. In addition, REEs contents in phosphorite may be extracted as a by-product during phosphoric acid production [4].

**Table (7): Concentration of Rare earth elements (ppm) of lower oxidized phosphorite, Siiya area, Nile Valley, Egypt**

Sec. No	S.N.O	LREES														$\Sigma$ LREES	$\Sigma$ HREES	$\Sigma$ REES
		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	TM	Yb	Lu			
1	4	69.2	90.3	12.1	53.1	12.3	3.2	4.9	0.6	4.2	1.2	3.2	0.5	2.1	0.3	245.1	12.1	257.2
2	11	51.5	77.1	7.6	37.3	5.9	1.9	9.8	1.2	9.3	2	5.7	1.1	6.7	1.2	191.1	27.2	218.3
2	12	49.1	98.1	8.1	32.7	7.9	2.1	10.3	1.1	9.1	2.3	6.2	0.9	5	0.6	208.3	25.2	233.5
2	14	61.2	87.2	13.2	66.3	12.8	3.5	12.6	2.3	12.6	1.8	5.9	1.2	6.9	0.9	256.8	31.6	288.4
2	15	53.1	89.7	7.8	38.9	8.7	2.9	9.9	0.9	11.3	2.1	6.1	1.1	5.2	0.7	211	27.4	238.4
3	19	48.3	66.3	12.2	41.3	12.1	2.1	11.7	1.2	8.6	0.9	5.9	0.4	6.2	1.1	194	36	230
3	21	50.4	69.1	9.3	37.1	6.2	3.5	7.5	0.6	5.3	1.3	2.3	0.6	2.6	0.5	183.1	20.7	203.8
3	22	53.6	90.4	8.6	49.3	7.9	1.1	12.1	1.2	9.5	1.8	6.3	1.2	4.3	0.9	223	25.2	248.2
5	32	37.1	61.2	11.4	31.2	5.9	0.9	5.9	0.8	4.2	1.2	3.4	0.7	2.9	0.5	153.6	198	173.2
5	33	49	78.5	6.9	49.5	13.2	3.2	6.1	1.4	8.1	1.4	5.4	0.5	5.8	0.8	206.9	23.4	229.8
5	34	46.2	37.1	11.3	33.4	6.3	1.3	13.2	1	6.8	1.7	3.9	1.2	4.7	0.6	148.8	19.9	168.7
6	38	66.1	79	5.9	30.2	14	2.8	8.9	2.6	10.2	2.4	5.8	0.4	6.5	0.3	206.9	28.2	235.1
6	39	63.2	96.2	7.6	61.3	11.8	1.9	12.7	1.3	13.5	1.7	6.7	0.9	7.8	1.2	254.7	33.1	287.8
6	40	78.3	89.3	8.3	39.7	10.9	3.2	9.2	2.8	14.8	2.5	7.6	0.8	9.4	0.7	238.9	38.6	277.5
6	43	71	69	8.6	25.1	4.1	2.6	10.3	1.9	15.1	2.2	5.5	0.3	7.1	1.3	190.7	33.4	224.1
Min.		46.2	37.1	5.9	25.1	4.1	0.9	4.9	0.6	4.2	1.2	2.3	0.3	2.1	0.3	148.8	12.1	168.7
Max.		78.3	98.1	13.2	61.3	13.2	3.5	13.2	2.8	14.8	2.5	7.6	1.2	9.4	1.3	256.8	38.6	288.4
Ave.		56.4	78.5	9.2	41.7	9.3	2.4	9.6	1.3	9	1.7	5.3	0.7	5.5	0.7	207.4	26.7	234.2

**Table (8): Concentration of Rare earth elements (ppm) of lower non-oxidized phosphorite, Sibiyaarea, Nile Valley, Egypt**

Sec. No	S.N.O	LREES														$\Sigma$ LREES	$\Sigma$ HREES	$\Sigma$ REES
		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	TM	Yb	Lu			
1	1	48	89.3	10.7	45.3	5.8	1.9	6.5	1	7.5	1.2	4.6	0.6	4.3	0.4	207.7	19.6	227.3
1	2	47	58.4	6.2	34.6	8.7	2.1	8.4	0.9	6.9	2.1	6.1	0.9	6	0.7	165.5	23.6	189.1
1	5	61.7	87.6	7.1	61.3	11.2	2.4	9.9	2	9.4	1.9	5.9	1.1	5.8	1	241.2	27.1	286.3
1	6	51	49.3	9.8	63.4	5.9	2	11.2	0.9	10.2	1.4	6.5	1.2	7.1	0.9	192.8	27.3	220.1
4	26	63	92.1	6.1	60.8	12.1	3.2	13.2	1.9	12.3	2.2	7	1.4	8.3	0.6	250.7	33.7	284.4
4	27	29	44.2	6.8	23.5	6.3	0.9	7.2	0.7	1.9	0.9	2.7	0.4	2.2	0.3	118.2	9.1	127.3
Min.		29	44.2	6.1	23.5	5.8	0.9	6.5	0.7	1.9	0.9	2.7	0.4	2.2	0.3	118.2	9.1	127.3
Max.		63	92.1	10.7	63.4	12.1	3.2	11.2	1.9	12.3	2.2	7	1.4	8.3	1	250.7	33.7	268.3
Ave.		50	70.1	7.7	48.1	8.3	2	9.4	1.2	8	1.6	5.4	0.9	5.6	0.6	196	23.4	222.4



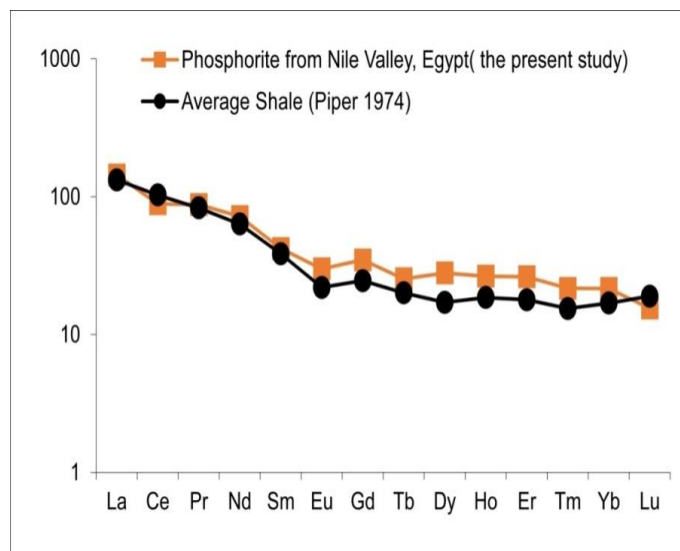
In the present study, representative samples from Nile Valley phosphorites are subjected to chemical analysis to determine the concentration and average abundance of REEs in the studied phosphorites (Tables 7 and 8). The total rare earth elements ( $\Sigma$ REEs) content in oxidized phosphorites falls in the range 168.7 ppm to 288.4 ppm with an average of about 234.2 ppm. In non-oxidized phosphorites, it attains value ranging from 127.3 to 286.3 ppm with an average of about 22.4 ppm (Tables 7 and 8). Light rare earth elements (LREEs) represent more than 85% of the total rare earth elements; where its content ranges from 148.8 to 256.8 ppm with an average of about 207.4 ppm for oxidized phosphorites and 118.2 to 250.7 ppm with an average of about 196.0 ppm for non-oxidized phosphorites. On the other hand, heavy rare earth elements (HREEs) represent less than 15% of the total rare earth elements; where its content at oxidized phosphorites ranges between 12.1 and 38.6 ppm with an average of about 26.7 ppm and 9.1 to 33.7 ppm with an average of about 23.4 ppm for non-oxidized phosphorites. Generally the total of REEs content in present phosphorite of Sibaiya area, Nile Valley is 228.3 ppm which is lower than Abu Tartur phosphorite (1718 ppm) [8]. Altschuler et al. [33] attributed the variations in the rare earth element content within different types of phosphorites to the varying depositional conditions. The interpretation of the REEs distribution in sediments is aided by their normalization to the world average of shale rather than chondrite because of the relative concentrations of REEs in sediments is very different from those in the chondrite. Normalization to chondrite, therefore, stresses these differences rather than displaying the smaller but more significant differences between sediment samples [34,35].

### 5.3.1 Chondrite-normalization patterns

The REEs patterns along both sides of the Nile Valley phosphorites and the world average shale [35] were normalized to the chondrite REEs concentrations [36] (fig 11). From this Figure, it can be observed that:

The phosphorites patterns exhibit LREEs enrichment relative to HREEs and slight negative Ce and Eu anomalies. The LREEs enrichment relative to HREEs in the studied phosphorites reflects post depositional modification of the REEs distribution in these deposits [37]. The slight negative Ce and Eu anomalies in phosphorites revealed their marine origin as well as the prevailing of reducing conditions during their formation.

2-The distribution pattern of the studied phosphorite is in relative harmony with that of world average of shale. This may suggest that the REE were derived from the associated clastic debris by diagenetic remobilization [38].



**Fig. (11): Chondrite normalized pattern of REEs from phosphorite, Nile Valley, Egypt and world average of shale [35]**

### 5.4. Radioactive elements

Marine phosphorites are considered as a good source of uranium where, they contain a value between 50-200 ppm, which represents 15 to 60 times greater than that of crustal abundances [13]. The phosphorite ores contain about 1500 Bq/kg activity concentration of uranium and radium [39]. The phosphorite are extensively used for fertilizers and phosphoric acid manufacturing where the majority of original uranium content is delivered into the fertilizers while lesser concentrations of  $^{226}\text{Ra}$  and  $^{232}\text{Th}$  are also received by the fertilizers [40]. Zidan [8] indicated that the Sibaiya phosphorite or the manufactured phosphatic fertilizers can impose radioactive risks for the environment and users.

The Radioactive elements of Sibaiya phosphorite of the Duwi Formation are given in Tables 9 and 10. The results showed that the studied phosphorite deposits are enriched in U and Ra relative to low Th contents. The U content in the oxidized phosphorite ranges from 50 to 135 ppm with an average value of 69 ppm. Meanwhile in the non-oxidized phosphorite it ranges from 48 to 118 ppm with an average value of 85 ppm. The eRa content in the oxidized phosphorite ranges from 46 to 89 ppm

with an average value of 63 ppm, while in the non-oxidized phosphorite it ranges from 46 to 74 ppm with an average value of 55 ppm.

Generally, the average U content in the studied non-oxidized phosphorite (85 ppm) is higher than oxidized phosphorite (69 ppm). Meanwhile, the average U of Helal phosphorite is 69 ppm [7], Red Sea phosphorite is 68 ppm [14] and Abu Tartur phosphorite is 23 ppm [24]. On the other hand, the average eRa content in the non-oxidized phosphorite (55 ppm) is lower than oxidized phosphorite (63 ppm). Whereas the average eRa of Helal phosphorite is 70 ppm [7], Red Sea phosphorite is 69 ppm [14] and Abu Tartur phosphorite is 26 ppm [24] as shown in (Table 11). Traditionally, the variation in U content is probably related to depositional and diagenetic aspects.

The eU/eTh ratio in the oxidized phosphorite ranges from 14 to 51 with an average of 27 ppm that indicates an addition of uranium to the area. The mobilization of uranium can be calculated from the equation: eU mob. =

eU – (eTh/3.5), which is the value of eU mobilization (eU mob). It ranges from 49 to 134 with an average of 81 (Table 7). Figure (10) shows direct relation between eU and eU/eTh ratio. The eU mobilization and chemical U shows a reverse relation with eTh/eU. On the other hand, the eTh shows a reverse relation only with eU/eTh and a direct relation with all the other parameters. This correlation supports the conception of uranium redistribution, especially in the oxidized phosphorite of Duwi Formation in the studied area where the correlation seems to be relatively stronger.

The eU/eTh ratio in the non-oxidized phosphorite ranges from 53 to 120 with an average of 36 which indicates an addition of uranium to the area. The value of mobilization (eU mob.) ranges from 50 to 119 with an average of 87, and this also shows enrichment of uranium in the Sibaiya area (Table 10). Figure (12) shows direct relations between eU and all parameters except eTh/eU ratio. The eTh shows direct relation with all the parameters except with eU/eTh which shows reverse relation.

**Table (9): Concentrations of radionuclides elements (ppm) of oxidized phosphorite of the Duwi Formation, Sibaiya area Nile Valley, Egypt**

Sec. No.	S.NO.	Uc	eU	eTh	eRa	eU/eTh	eTh/eU	eU/eRa	eTh/eRa	eUmob.
1	4	65	69	4	52	17	0.06	1.3	0.08	68
2	11	88	90	4	53	23	0.04	1.7	0.08	89
2	12	69	71	5	56	14	0.07	1.3	0.09	70
2	14	69	71	5	56	14	0.07	1.3	0.09	70
2	15	50	51	1	46	51	0.02	1.1	0.02	51
3	19	64	66	4	59	17	0.06	1.1	0.07	65
3	21	50	51	1	46	51	0.02	1.1	0.02	51
3	22	90	92	6	63	15	0.07	1.5	0.10	90
5	32	74	82	6	89	14	0.07	0.9	0.07	80
5	33	112	115	3	76	38	0.03	1.5	0.04	114
5	34	105	111	6	63	19	0.05	1.8	0.10	109
6	38	79	82	5	65	16	0.06	1.3	0.08	81
6	39	132	135	3	84	45	0.02	1.6	0.04	134
6	40	85	89	2	78	45	0.02	1.1	0.03	88
6	43	48	50	2	53	25	0.04	0.9	0.04	49
Min.		48	50	1	46	14	0.02	0.9	0.02	49
Max.		132	135	6	89	51	0.07	1.8	0.10	134
Ave.		79	82	4	63	27	0.05	1.3	0.06	81

eU= equivalent uranium

Uc= chemical uranium

**Table (10): Chemical analysis of radionuclides (ppm) of non-oxidized phosphorite of the Duwi Formation, Sibaiya area, Nile Valley, Egypt**

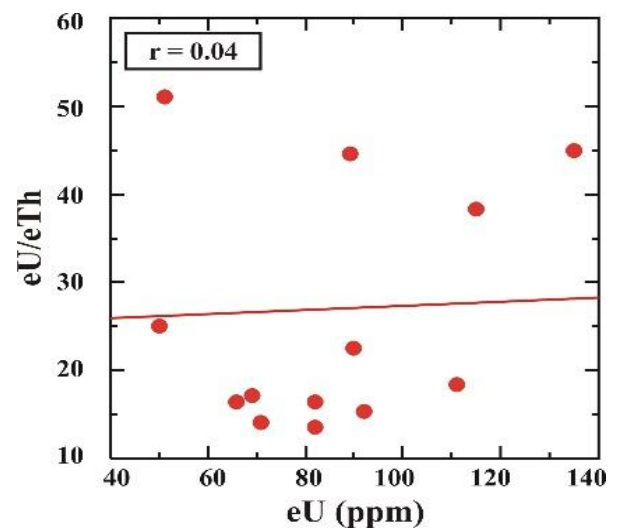
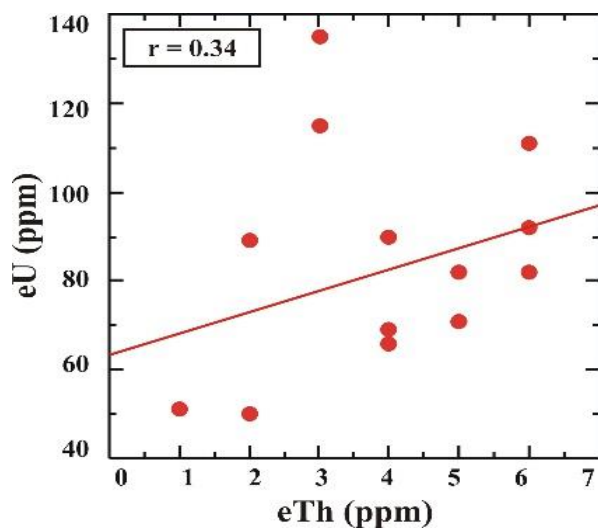
Sec. No.	S.NO	Uc	eU	eTh	eRa	eU/eTh	eTh/eU	eU/eRa	eTh/eRa	eUmob.
1	4	99	102	5	73	20	0.05	1.4	0.07	102
2	11	80	84	3	46	28	0.04	1.8	0.07	83
2	12	115	117	5	74	23	0.04	1.6	0.07	116
2	14	50	53	1	46	53	0.02	1.2	0.02	53
2	15	118	120	3	46	40	0.03	2.6	0.07	119
3	19	48	50	1	46	50	0.02	1.1	0.02	50
Min.		48	50	1	46	20	0.02	1.1	0.02	50
Max.		118	120	5	74	53	0.05	2.6	0.07	119
Ave.		85	88	3	55	36	0.03	1.6	0.05	87

eU=equivalent uranium

Uc= chemical uranium

**Table (11): Average of U, Th and eRa content (ppm) of Sibaiya phosphorite compared to some published data in Egypt**

Trace element	Oxidized Sibaiya phosphorite	Non-oxidized Sibaiya phosphorite	Helal phosphorite[7]	Abu Tartur phosphorite[24]	Red Sea Phosphorite[14]
U	69	85	69	23	68
eTh	4	3	2	3	4
Ra	63	55	70	26	69





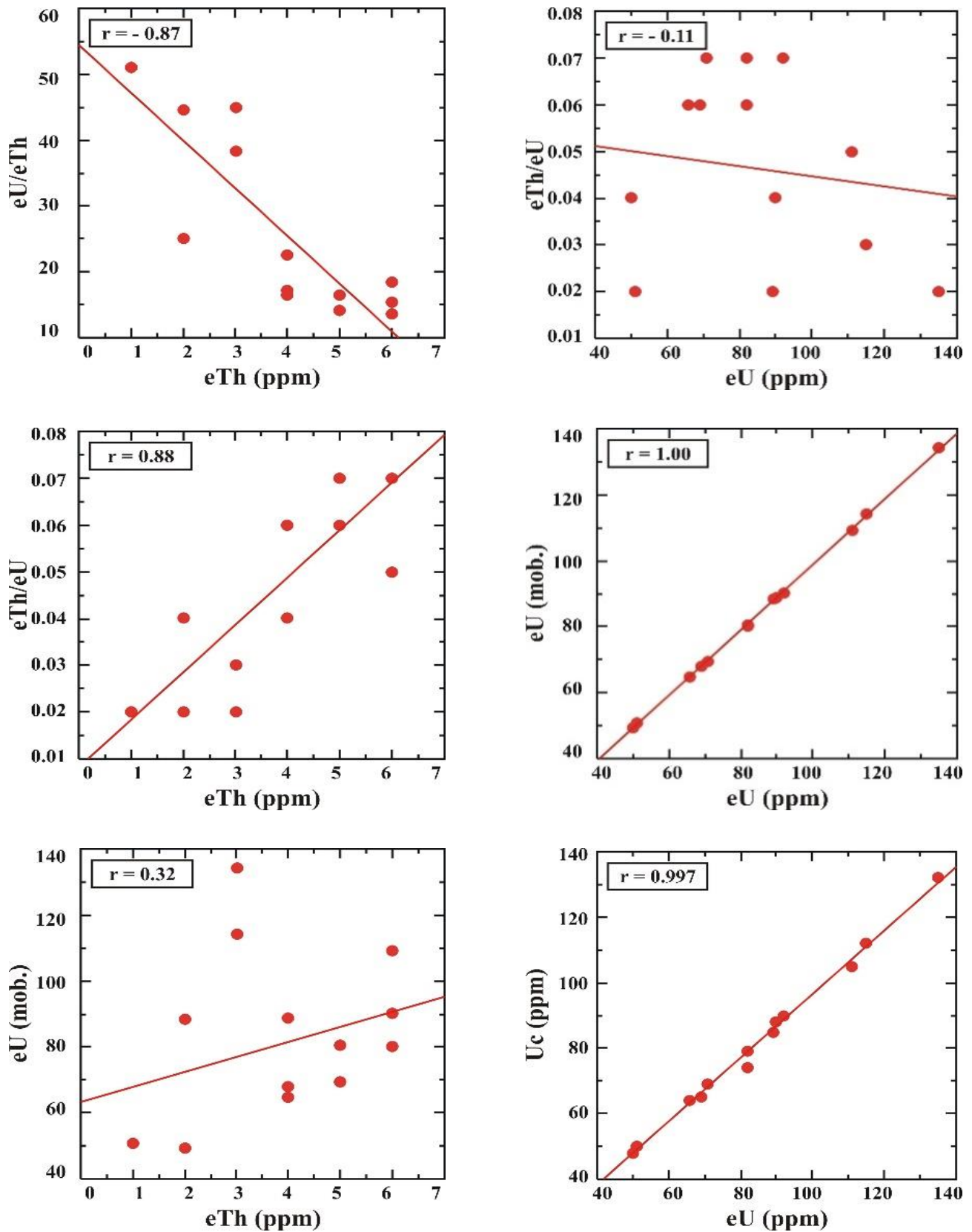
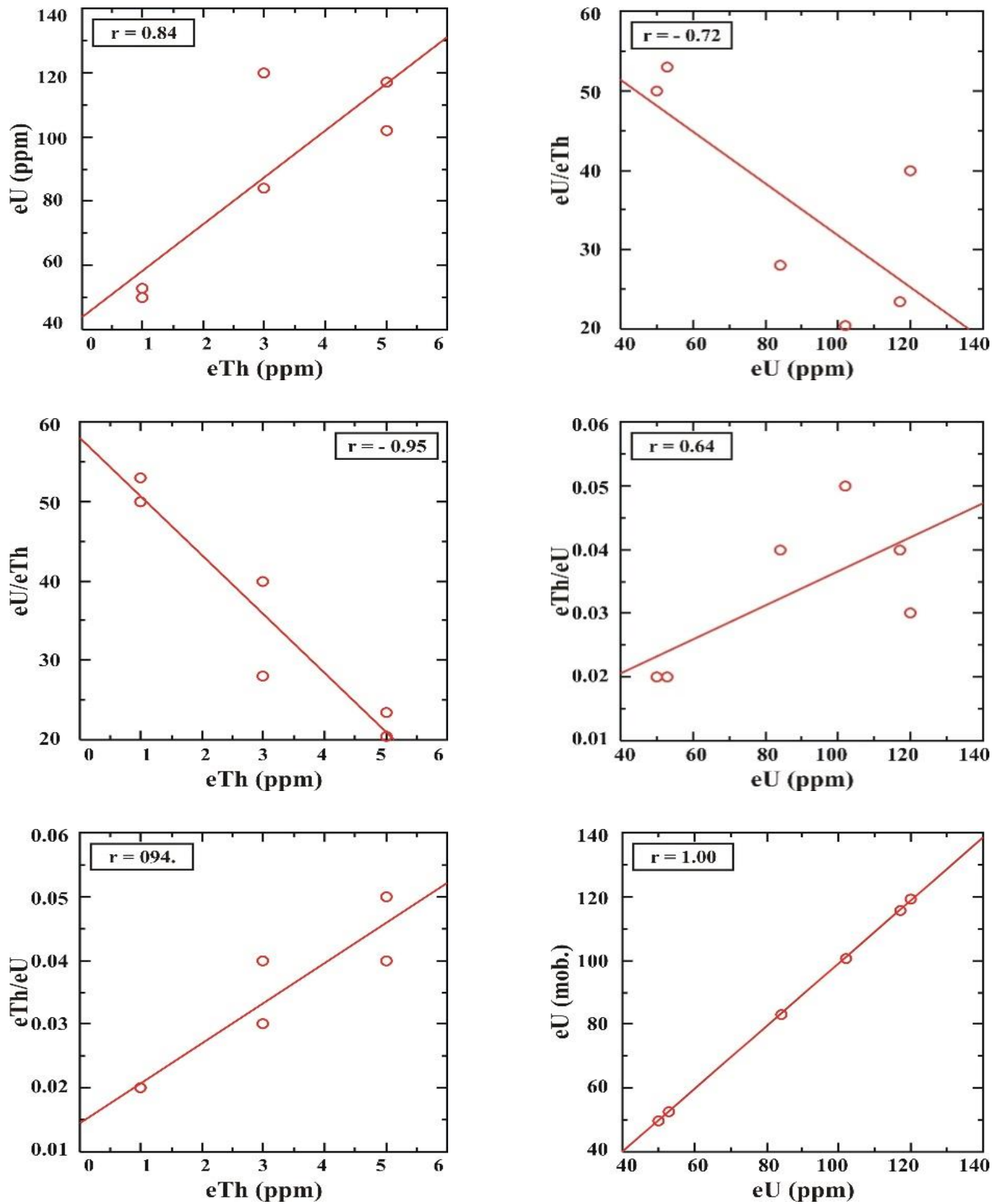
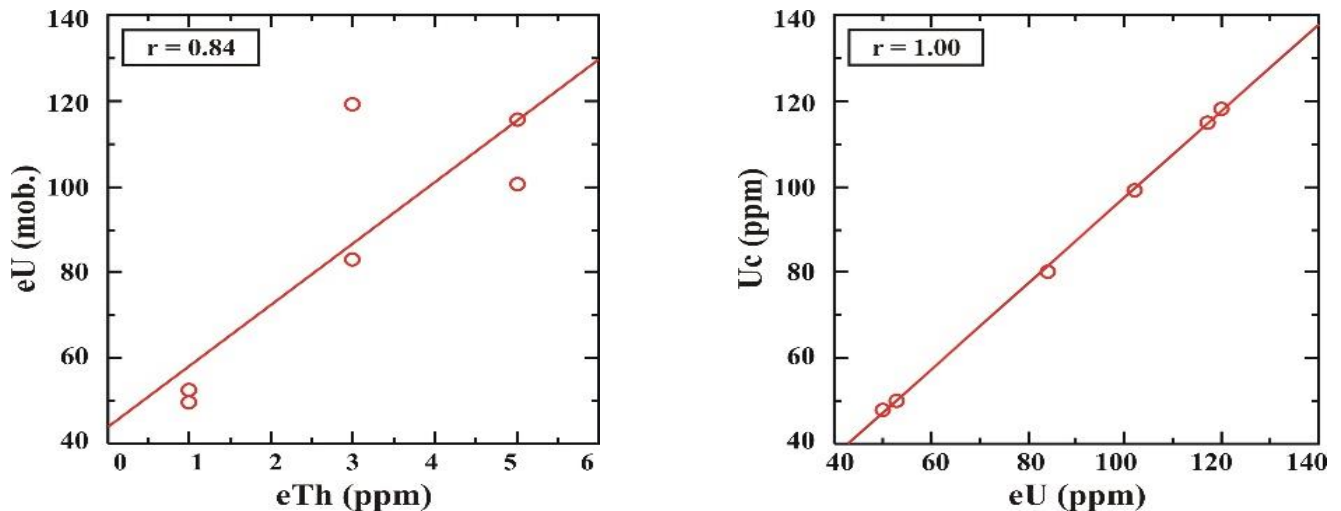


Fig. (12): The relations between eU and eTh, eU and eU/eTh, eTh and eU/eTh, eU and eTh/eU, eTh and eTh/eU, eU and eU mob., eTh and eU mob., and eU with U<sub>c</sub> for oxidized phosphorite of the Duwi Formation at Sibaiya area, Nile Valley, Egypt





**Fig. (13):** The relations between eU and eTh, eU and eU/eTh, eTh and eU/eTh, eU and eTh/eU, eTh and eTh/eU, eU and eU mob., eTh and eU mob., and eU with Uc for non-oxidized phosphorite of the Duwi Formation at Sibaiya area, Nile Valley, Egypt

## 6. CONCLUSIONS

Litho-stratigraphic successions of Sibaiya area comprise the Qussier shale member un-conformably overlain by the Duwi Formation which is consisting of lower, middle and upper phosphorite members conformably followed upward by the Dakhla Formation. The lower member is considered as the economic productive phosphorite beds in Sibaiya area. The lower phosphorite member consists of a moderately hard oxidized phosphorite with yellowish to brown colour and non-oxidized phosphorite in some parts with grey color. The average thickness of this member is 3.40 m in west Sibaiya, while its maximum average thickness is 4.8 m in east Sibaiya. Petrography, phosphate beds are consist of phosphatic particles (Peloid grains, Bioclasts and Coprolites) and Non-phosphatic particles represented by dolomite, Calcite, hematite, Pyrite, gypsum, strontianite and detrital quartz as matrix and cement materials. The average total rare earth elements ( $\Sigma$  REEs) content in oxidized phosphorites is 234.2 ppm, while in non-oxidized phosphorite it is 222.4 ppm. Generally the total REEs content in present phosphorite of Sibaiya area, Nile valley is 228.3 ppm. The average of  $P_2O_5$  and U contents in oxidized phosphorite are 24.18 % and 69 ppm respectively, meanwhile in non-oxidized phosphorite, they are 27.8 % and 85 ppm respectively. Sibaiya phosphorites are considered as medium grade for oxidized phosphorite and high grade for non-oxidized phosphorite. Generally, the Sibaiya area could provide an economic value for production of phosphoric acid and extracted of U as by-product.

## RECOMMENDATION

The phosphorites of Sibaiya area are recommended to be suitable for mining and production of phosphoric acid more than phosphatic fertilizers due to its higher radioactivity relative to Abu Tartur and Red Sea phosphorites as well as the U can be extracted as by-product.

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