A CONTRIBUTION TO THE GEOCHEMISTRY OF EL-SIBAIYA PHOSPHORITES, NILE VALLEY, EGYPT

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ABSTRACT

El-Sibaiya phosphorites represent a part of the Middle East to North Africa phosphogenic province. They encountered in the Gabal (G.) Duwi Formation of Late Cretaceous to Paleogene age. The studied samples have been collected from the eastern and western sides of the Nile River.

Major elemental analysis of the collected samples declared positive correlations between P_2O_5 and CaO and F. These correlations indicate that these elements are contained in the apatite phase. On the other hand, P_2O_5 shows negative correlations with other major elements such as Al_2O_3, SiO_2, Fe_2O_3 and MgO. Some trace elements such Cr, Sr and V show positive correlation with P_2O_5.

The average of the total rare earth elements ($\sum$REEs) in the studied phosphorites is 262ppm. Chondrite-normalized patterns of $\sum$REEs of the studied phosphorites show a good coherence with the world average of shale suggesting that $\sum$REEs in the studied phosphorites were derived from the associated clastic debris through the diagenetic remobilization. The week negative Ce and Eu anomaly of the studied samples and the marked enrichment in LREEs emphasize that the studied phosphorites subjected to a later post-depositional modification.

Laser ablation analysis showed that apatite mineral of the studied phosphorites is enriched in some elements such as Ca, F, Cr, Sr, V, Zn, Ba and REEs. This explains the major role of substitution processes of these elements within apatite lattice.

The uranium average in El-Sibaiya East phosphorites is 81.6 ppm, while in El-Sibaiya West is 51.1ppm. Apatite minerals play an important role in the accumulation of U within the studied phosphorites.

INTRODUCTION

Phosphorites are one of the important economic deposits in the world as they are the raw material for many important industries. They represent the host rock for some strategic elements especially REEs, uranium, thorium and fluorides.

The geochemistry of phosphorites has been widely studied due to their economic importance (Jarvis et al., 1994). The chemical composition of apatite mineral is highly variable because its crystal structure allows a variety of substitutions (McClellan and Lehr, 1969). Variability in chemical composition of apatite may reflect difference in original composition, modification during diagenesis, or modification during weathering (Jarvis et al., 1994).

Some of previous studies on the Nile Valley phosphorites are summarized within

here;

Ghanem et al. (1968) stated that the Nile Valley phosphorites can be divided into three groups according to P_2O_5 content: a) Phosphateores, b) Poor-phosphates, c) Phosphate-free rocks.

El-Kammar (1970) studied the Egyptian phosphorites and reported that the phosphate and carbonate fractions of the Nile Valley phosphorites are enriched in P, Ca, Mg, Fe, Na, Mn, Cu, Pb, Ag, Zn, Gd, Y, Yb, Be, U, Sr and Ni, whereas the detrital components have high amounts of Si, Al, K, Cu, Pb, Zn, Zr, Ga, Sn, Ti, Cr, V, Ba, Co and Ni,

Cook (1972) classified the source of trace elements in phosphorites into four categories: 1) trace elements associated with the detrital minerals, 2) trace elements introduced by weathering, 3) trace elements incorporated with the organic matter and 4) trace elements located within the apatite lattice.

Germann et al. (1984) stated that the Egyptian phosphorites are mainly composed of phosphatic minerals francolite and dahllite and non-phosphatic varieties represented by dolomite, calcite, quartz, kaolinite and illite, as well as the gangue minerals pyrite, gypsum and anhydrite.

Jarvis et al. (1994) concluded that Rare earth elements (REEs) concentrations with their characteristic patterns and Ce and Eu anomalies in the marine phosphorites are useful indicators of their marine depositional environments.

Picard et al. (2002) reported that phosphorites commonly display highly variable REEs patterns due to the variations in the composition and amount of associated detritus, depositional environment, sea- and pore-water redox, pH, age and water depth.

Baioumy et al. (2007) recognized that the Egyptian phosphorite occurs mainly as carbonate fluorapatite (francolite).

Baioumy (2011) stated that the negative Ce and Eu anomalies of the upper Cretaceous phosphorites in Egypt reflect their formation under reducing conditions with some evidences of post-depositional modifications of these elements.

This work aims to study the mineralogy and geochemistry of El-Sibaiya phosphorites. The importance and possible controlling factors of the elemental variability among the studied phosphorites are also discussed. To achive this objective, a combination of mineralogical and geochemical analyses has been carried out.

GEOLOGIC   SETTING

The studied phosphorites occur in the Upper Cretaceous Duwi Formation (Said, 1990). The Duwi Formation unconformably overlies the Middle Campanian Qusier shale and conformably underlies the middle Maastrichtian-Dakhla shale (Said, 1990).

The Duwi Formation represents the establishment of the first fully marine condition that extended across Egypt during the major transgression in Late Cretaceous time (Glenn and Arthur, 1990).

The studied phosphorites occur along the eastern side (El-Sibaiya East) and the western side (El-Sibaiya West) of the Nile River (Fig. 1).

This Formation is mainly composed of phosphorite beds intercalated with shale, marl, oyster limestone and chert bands (Fig. 2).

The studied phosphorite succession has been subdivided into three horizons: A, B and C (Fig. 2).

SAMPLES AND METHODS

Eleven bulk phosphorite samples were collected from the economic bed (horizon A) of the Duwi Formation from El-Sibaiya East and El-Sibaiya West.
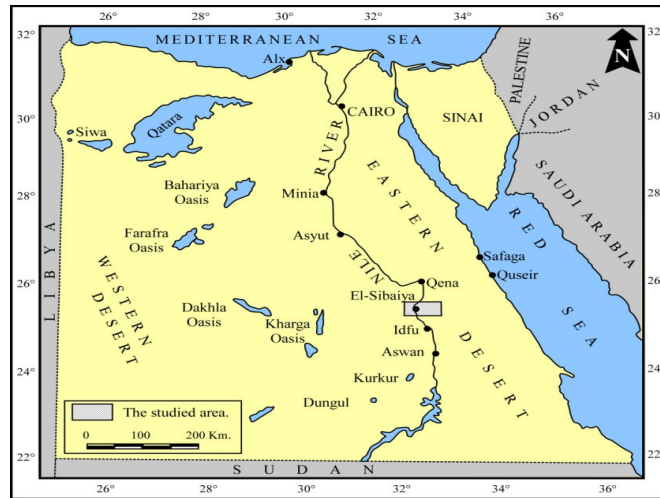
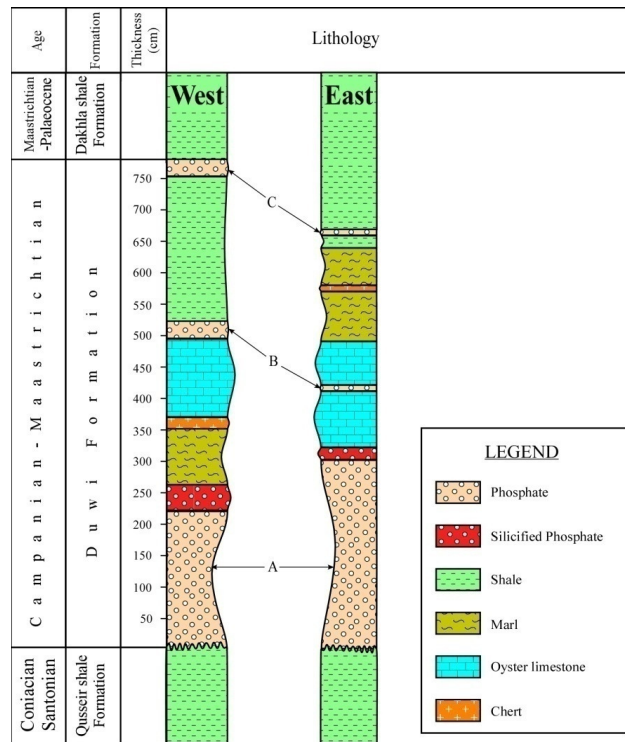Fig. 1: Key map showing the location of the studied area

Fig.2: Lithostratigraphic composite succession of Duwi Formation in the studied localities

The major oxides (P_2O_5, CaO, Fe_2O_3, MgO, SiO_2, Al_2O_3, Na_2O, K_2O, TiO_2 and F) were estimated using the conventional wet chemical techniques of Shapiro and Brannock (1962), with some modifications given by El-Reedy (1984). The concentrations of major oxides were measured using UNICAM spectrophotometer, JENWAY flame photometer and SCHOTT titrimetric technique using EDTA.

The X-ray fluorescence technique was used to determine some trace elements content (Cr, Ni, Cu, Zn, Zr, Rb, Y, Ba, Sr and V) within the studied samples. This technique was carried out using PHILIPS Unique-II spectrometer equipment with the automatic sample changer PW 1510, (30 positions). It is connected to a computer system using X-40 program for spectrometry.

X-ray diffraction technique (XRD), was used to identify the unknown minerals using PHILIPS PW 3710/31 diffractometer, scintillation counter, Cu-target tube and Ni filter at 40 kV and 30 mA.

These analyses were carried out through the laboratories of the Egyptian Nuclear Materials Authority (NMA).

The rare earth elements content were determined using the ICP-MS and laser ablation at the laboratories of Senckenberg Research Institute in Dresden, Germany. This technique was carried out using Excimer-Laser (UP 193, New Wave) and ICP-MS (Element 2XR, ThermoFisher)

RESULTS

Mineralogy and Petrography

The mineralogy of El-Sibaiya phosphorites was mainly investigated by X-ray diffraction (XRD), the obtained data revealed that the examined samples are composed essentially of phosphate and non-phosphate minerals.

Carbonate-flourapatite (francolite) $Ca_5[(PO_4,CO_3)_3|(F,O)]$ is the most abundant variety of apatite minerals in the studied phosphorite. The main characteristic d-spacing of francolite is (2.79-2.80 Å, 2.69-2.70Å and 2.62-2.63 Å) have been detected in the patterns of the analyzed samples (Fig.3). Carbonate-hydroxyl apatite (dahllite) $Ca_5[(PO_4,CO_3)_3|(OH,O)]$ can uncommonly be detected in some samples.

Quartz occurs as detrital grains that enclosed within phosphatic peloids or embedded in the groundmass. It is more abundant in the silicified phosphatic samples. Its characteristic reflections in the XRD patters are 3.34Å (100%), 4.26Å (35%) and 1.82Å (17%). Calcite occurs as cement as well as allochemcs and mainly oyster limestone shells. Calcite identified in the XRD patterns at 3.035Å (100%), 2.095Å (18%), 2.285 Å (18%) and 3.86Å (12%). Gypsum is characterized in the XRD patterns by 7.56Å (100%), 3.06Å (55%) and 4.27Å (50%), (Fig. 3).

The petrographic studies declared that the studied phosphorites are composed mainly of phosphatic and non-phosphatic constituents (Fig.4). The phosphatic constituent represents 65 to 80% by volume of the whole studied rock, they are classified into phosphatic mudclasts (collophane grains) and phosphatic bioclasts (fish bones and sharks teeth). Detrital quartz grains, carbonates as shell fragments as well as iron oxides are the main non-phosphatic constituents of the phosphorites.

Montmorillonite with its reflections 14.92 Å, 15.58 Å, 12.41 Å and 4.48 Å, 4.49 Å, 4.46 Å and kaolinite with the 7.20 Å, 7.15 Å, 7.22 Å and 3. 58 Å, 3.59 Å, 3.59 Å are the predominated clay minerals in the studied phosphorites (Fig.5).

Geochemistry

The studied phosphorites were examined through detailed chemical investigations to determine the major, trace and rare earth elements composition and declaring the interrelationships between them. The resultant data are listed in Tables (1-6).
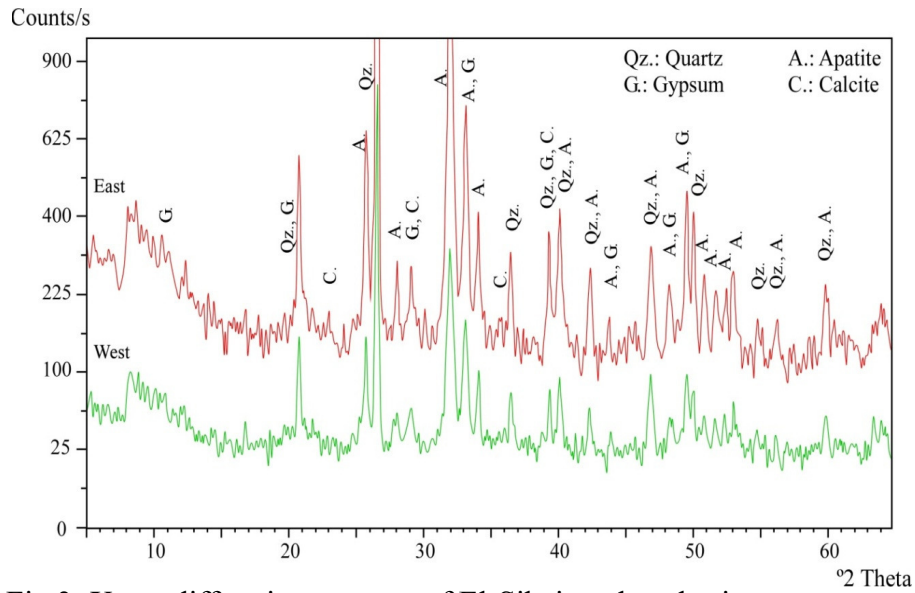
Fig.3: X-ray diffraction patterns of El-Sibaiya phosphorites

Fig.4: Photomicrograph of a thin section showing elongated cryptocrystalline homogeneous pellet (P) of collophane rimed by some phosphatic bone fragments (XPL)
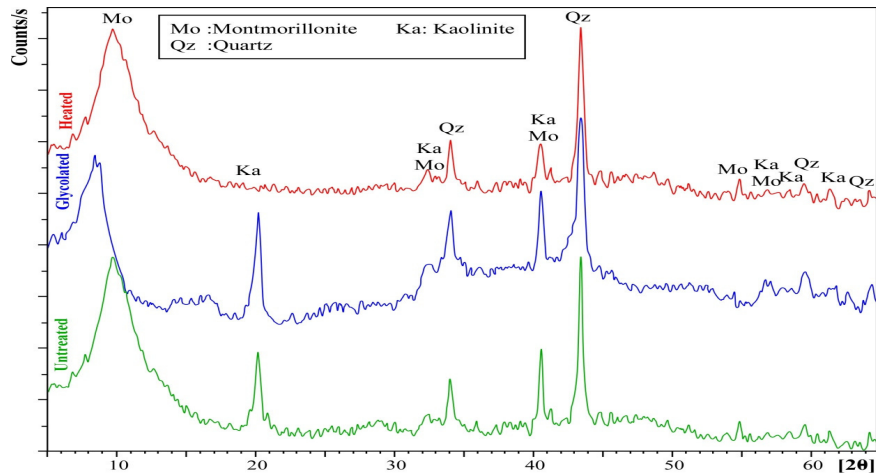
Fig.5: X-ray diffraction patterns of clay minerals associated with El-Sibaiya phophorites

Major elements

Phosphorus and calcium oxides

Phosphorus contained mainly in apatite. P_2O_5 average content in the studied samples are 27.60% and 23.12% for the eastern side and western side, respectively (Tables 1&2).

Calcium occurs as phosphates, carbonates and/or sulfates. CaO content in the studied samples is nearly the same along the two sides of El-Sibaiyawith an average of about 40%.

Fluorine

Fluorine average content is 2.25 % for the eastern side phosphorites and 2.19% for the western side phosphorite (Tables 1&2).

Iron oxide

The total iron in the studied phospho- riteswas determined as Fe_2O_3. Fe_2O_3 content in the eastern side phosphorites has an aver- age of about 4.12%, while in the western sid- edecreased to be 2.98% (Tables 1&2)..

Silicon oxide

SiO_2 content in the eastern side phospho- riteshas an average of about 9.98%. Whereas its average content   increased in the western side phosphorites up to 18.50% (Tables 1&2).

The high SiO_2 ratio can be attributed to the presence of   quartz grains, silica cement and/or clay in the bulk samples.

Aluminum oxide

Al_2O_3 in the eastern side   phosphorites has an average of about 3.48%. It decreases to be 1.29% in the western sidephosphorites (Tables 1&2). This is due to the associated clay min- erals which identified by XRD analysis.

Magnesium oxide

MgO content in the eastern side phospho- rites has an average of about 3.01%, whereas in the western side it decreases to 2.75%. Part of this ratio may occur as a main constituent in some clay minerals as montmorillonite and kaolinite.

Sodium and potassium oxides

Na_2O content of the eastern side phos- phorites has an average of about 1.25%, that decreases to 0.85% in the western side phos- phorites. K_2O content has an average of about

Table1: Major oxides concentrations of the eastern side phosphorite

Oxide Sample	P₂O₅	CaO	Fe₂O₃	MgO	SiO₂	Al₂O₃	Na₂O	K₂O	TiO₂	F	L.O.I. 110°C	550°C	1000°C
1E	25.14	39.82	4.79	2.82	10.53	4.43	0.97	0.25	0.01	2.20	0.79	2.49	5.62
2E	27.60	39.35	4.39	2.02	11.50	2.65	1.34	0.82	0.01	2.35	0.79	2.34	5.67
3E	31.72	40.84	3.99	2.23	7.63	3.62	1.23	0.24	0.01	2.41	0.57	2.18	3.74
4E	25.14	39.72	3.99	3.63	9.36	5.67	1.12	0.20	0.01	2.15	0.84	2.42	4.76
5E	24.15	38.11	3.79	3.84	11.36	5.10	1.37	0.26	0.01	2.31	1.08	2.58	5.62
6E	21.17	37.01	5.59	3.23	16.24	5.92	1.40	0.35	0.02	1.90	0.90	2.19	3.43
7E	32.16	41.86	3.19	3.27	7.66	1.58	1.34	0.28	0.02	2.27	0.59	2.41	3.45
8E	30.43	42.59	3.59	3.23	7.29	2.01	1.32	0.17	0.01	2.45	0.70	2.25	4.02
9E	27.31	43.44	3.19	3.23	9.53	2.56	1.23	0.15	0.02	2.25	0.49	2.19	5.23
10E	28.07	40.28	3.99	3.23	10.91	2.21	1.23	0.21	0.01	2.30	0.63	2.35	4.01
11E	30.72	41.20	4.79	2.42	7.80	2.56	1.18	0.19	0.01	2.20	1.05	2.15	3.64
Min.	21.17	37.01	3.19	2.02	7.29	1.58	0.97	0.15	0.01	1.90	0.49	2.15	3.43
Max.	32.16	43.44	5.59	3.84	16.24	5.92	1.40	0.82	0.02	2.45	1.08	2.58	5.67
Aver.	27.60	40.38	4.12	3.01	9.98	3.48	1.25	0.28	0.01	2.25	0.77	2.32	4.47

E = Eastern side

Table2: Major oxides concentrations of the western side phosphorite

Oxide Sample	P₂O₅	CaO	Fe₂O₃	MgO	SiO₂	Al₂O₃	Na₂O	K₂O	TiO₂	F	L.O.I. 110°C	550°C	1000°C
1W	24.05	40.60	3.99	2.23	16.40	1.26	1.17	0.10	0.11	2.25	0.45	2.52	4.53
2W	25.38	41.40	1.39	2.63	15.80	1.06	0.97	0.13	0.18	2.30	0.67	2.69	5.03
3W	24.70	39.60	3.29	3.63	15.10	1.12	1.07	0.14	0.15	2.21	0.47	2.45	5.81
4W	24.34	39.10	3.79	1.61	19.70	0.76	0.69	0.13	0.18	2.40	0.20	2.71	3.99
5W	19.75	40.70	3.07	1.61	19.70	2.25	1.10	0.14	0.15	1.90	0.24	2.34	7.80
6W	23.81	42.40	3.17	2.02	18.30	1.01	0.65	0.09	0.01	2.40	0.10	2.47	3.63
7W	21.74	37.40	2.79	2.42	24.72	0.65	0.69	0.09	0.06	1.95	0.09	2.11	6.20
8W	22.61	42.10	2.40	3.63	18.60	1.37	0.69	0.14	0.06	2.05	0.29	2.32	3.83
9W	17.18	31.90	4.19	3.80	29.63	2.10	0.90	0.10	0.31	1.95	0.10	1.75	6.38
10W	26.30	42.15	1.90	3.45	10.18	1.43	0.60	0.09	0.21	2.30	0.54	2.52	7.82
11W	24.43	39.20	2.79	3.23	15.39	1.24	0.80	0.09	0.03	2.20	0.24	2.27	7.34
Min.	17.18	31.90	1.39	1.61	10.18	0.65	0.60	0.09	0.01	1.90	0.09	1.75	3.63
Max.	26.30	42.40	4.19	3.80	29.63	2.25	1.17	0.14	0.31	2.40	0.67	2.71	7.82
Aver.	23.12	39.69	2.98	2.75	18.50	1.29	0.85	0.11	0.13	2.17	0.31	2.38	5.67

W = Western side

0.28% for the eastern side phosphorites decreasing to 0.11% in the western side phosphorites (Tables 1&2).

K_2O is essential constituent of the clay minerals where it is principally associated with aluminum in illite and/or illite-smectite mixed-layer clay minerals.

Trace elements
Chromium and vanadium

Chromium and vanadium have the same geochemical behavior in the studied phosphorites. McKelvey et al. (1953) suggested that Cr and V are shared between apatite and clays.

Chromium content in the studied samples is nearly the same along the two sides with an average of about 127ppm (Tables 3&4).

The phosphorites of the eastern side contain vanadium with an average of about 151 ppm, whereas in the western side vanadium has an average of about 104ppm.

Nickel

Nickel content in the studied samples is nearly the same along the two sides withan average of about 14ppm. The average of Cr/

Table 3: Trace elements concentrations of the eastern side phosphorite

Element	Cr	Ni	Cu	Zn	Zr	Rb	Y	Ba	Sr	V
1E	127	15	13	137	23	17	45	756	1265	159
2E	130	15	13	139	14	31	48	663	1319	171
3E	135	10	12	139	15	25	51	618	1742	170
4E	128	15	13	138	13	29	46	660	1248	150
5E	125	18	14	135	13	33	84	796	1167	147
6E	110	11	13	133	16	31	58	485	1610	128
7E	125	12	14	142	15	25	40	769	1812	170
8E	134	11	13	142	16	28	36	760	1558	133
9E	127	12	12	170	18	31	56	870	1615	128
10E	129	21	12	160	13	34	38	585	1401	140
11E	123	14	13	150	13	29	59	742	1717	167
Min.	110	10	12	133	13	17	36	485	1167	128
Max.	135	21	14	170	23	34	84	870	1812	171
Aver.	127	14	13	144	15	28	51	700	1496	151

E = Eastern side

Table 4: Trace elements concentrations of the western side phosphorite

Element	Cr	Ni	Cu	Zn	Zr	Rb	Y	Ba	Sr	V
1W	144	18	13	140	13	24	63	623	1220	117
2W	129	14	12	140	16	32	72	782	1348	117
3W	127	15	13	130	15	23	67	690	1283	113
4W	148	15	13	150	13	38	58	845	1098	119
5W	111	9	12	150	13	30	40	561	1219	107
6W	156	17	13	150	16	25	76	737	1153	133
7W	108	11	13	120	11	28	93	566	1126	63
8W	140	16	12	120	16	25	81	808	1273	106
9W	98	18	13	120	16	32	80	600	961	55
10W	130	8	12	140	11	18	54	623	1387	138
11W	120	10	13	110	16	36	78	860	1575	72
Min.	98	8	12	110	11	18	40	561	961	55
Max.	156	18	13	150	16	38	93	860	1575	138
Aver.	128	14	13	134	14	28	69	700	1240	104

W = Western side

Ni ratio in the studied phosphorites reaches nearly up to 9.14 suggesting their derivation from mafic volcanic sediments (Tables 3&4).

Copper

Copper content in the studied samplesis nearly the same along the two sides havingan average of about 13ppm (Tables 3&4).

Zinc

Zinc content in the studied phosphorites

of the eastern side has an average of about 144 ppm decreased to be 134ppm in the western side (Tables 3&4).

Zirconium

•Zirconium content in the studied samplesis nearly the same along the two sides having an average of about 14ppm.

Barium

•Barium content in the studied phospho-

rites is nearly the same along the two sides having an average of about 700 ppm.

Strontium

Strontium is strongly enriched in marine phosphorites, its average content in the eastern side phosphorites is 1496 ppm which decreases to 1240 ppm in the western side phosphorites (Tables 3&4).

Inter-elements relationships

The statistical treatment of analytical data of the studied phosphorites show positive correlation between P_2O_5 and other elements that located inside the apatite lattice such as CaO, F and Sr as expected. Meanwhile P_2O_5 shows negative correlation with some other elements that located outside the apatite lattice such as Fe_2O_3, SiO_2 and Al_2O_3 (Figs.6-13).

P_2O_5 shows positive correlation with some trace elements such as Cr, Sr and V. This positive correlation with P_2O_5 indicate the substitution of these elements in the apatite structure.

Rare earth elements

In the present work, ten representative bulk samples (five from each side) are subjected to chemical analysisusing the ICP technique to determine the concentrations and average abundances of the REEs (Table 5).

Total rare earth elements (ΣREEs) content in the eastern sidehave an average of about 274.8 ppm decreased to be 249.7ppm in the western side. Light rare earth elements (LREEs) represent more than 85% of the total rare earth elements with an average of about 244.7 ppm and 216.4 ppm for the eastern side and western side respectively. On the other hand, heavy rare earth elements (HREEs) represent less than 15% of (ΣREEs) with an average of about 46.6 ppm and 33.2 ppm for the eastern side and western side respectively.

The enrichment of the RREs in the studied phosphorites can be affiliated to the Sea
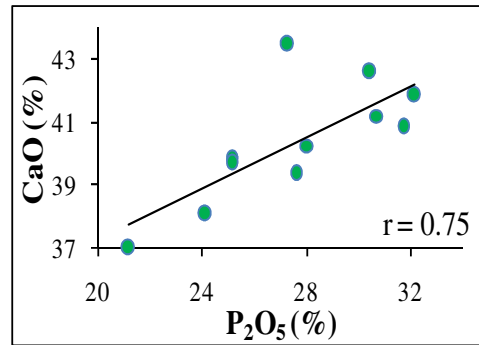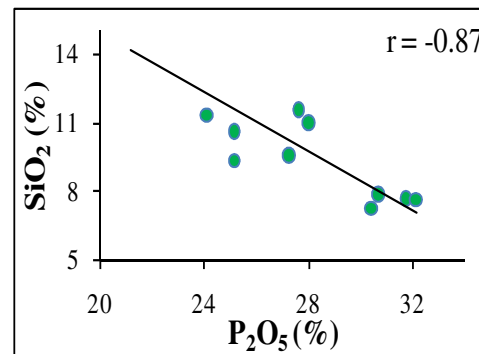

Fig.6: Correlation between P_2O_5 and CaO(%)
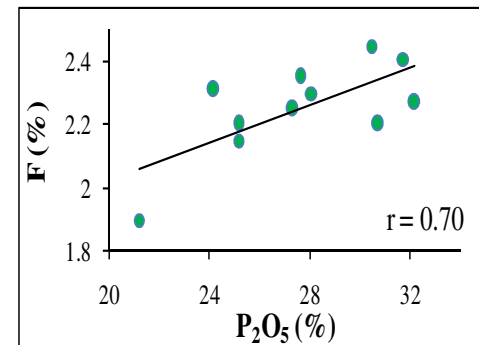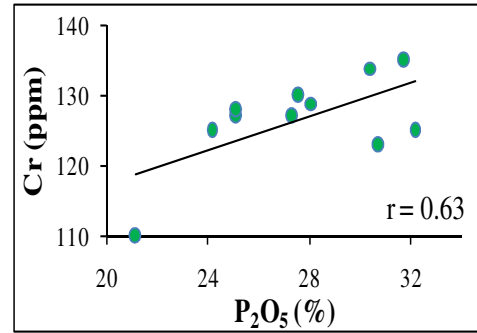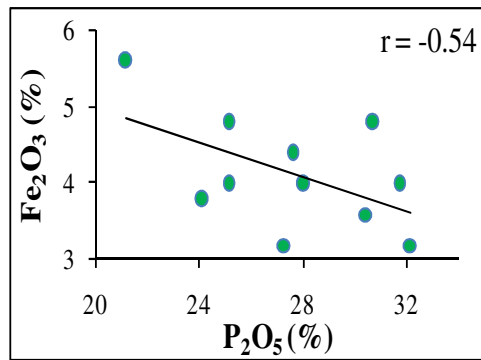

Fig.7: Correlation between P_2O_5 and SiO_2 (%)
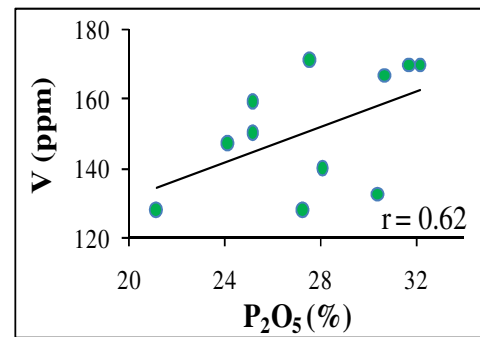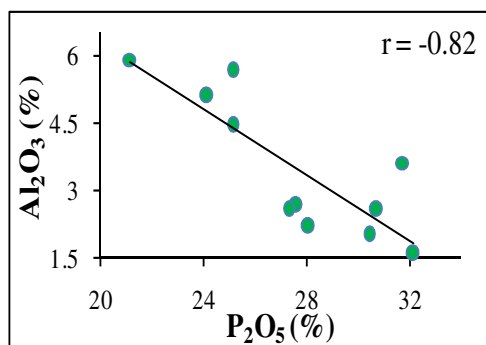

Fig.8: Correlation between P_2O_5 and F (%)
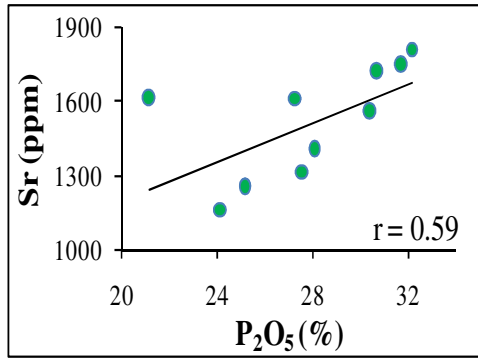
Fig.9: Correlation between P_2O_5 and Sr(ppm)

Fig.12:   Correlation between P_2O_5 and Cr(ppm)

Fig.10:Correlation between P_2O_5 and Fe_2O_3 (%)

Fig.13: Correlation between P_2O_5 and V(ppm)

Fig.11:Correlation between P_2O_5 and Al_2O_3 (%)

water enriched in REEs and the ability of apatite crystals to fix the REEs in its structure. According to McConnell (1973) and Grand-jean-Lecuyer et al. (1993), apatite and phosphate-rich faunal remnants (like fish teeth)that constitute these phosphorites can store high quantities of REEs due its unique crystallo-chemical properties.

Altschuler et al. (1967) attributed the variations in the rare earth elements content within the different types of phosphorites to the variation in depositional conditions.

Chondrite-normalization patterns

The REEs pattern (Fig.14) representing the average of both sides of El-Sibaiyaphos-

Table 5: Rare earth elements concentration (ppm)

|	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣLREEs	ΣHREEs	ΣREEs
6E	75.6	105.6	14.4	58.7	12.3	3.3	5.5	0.8	5.5	1.2	3.8	0.6	3.7	0.4	275.4	16	291.4
7E	56.5	77.2	9.2	40.8	7.6	2.1	10.1	1.5	10.9	2.7	7.5	1.1	7.7	1.1	203.6	32.6	236.2
8E	51	86.4	9.9	41.8	8.5	2.5	10.4	1.5	10.4	2.4	7.1	1	7	0.8	210.4	30.2	240.6
9E	66.2	110.3	16.1	70.7	14.6	3.9	15.9	2.2	14.7	2.9	7.9	1.2	7.3	0.9	297.7	37.1	334.8
10E	63.7	93.8	10.7	45.2	9.7	2.6	10.4	1.6	11.2	2.6	8.1	1.3	9.1	1.2	236.1	35.1	271.2
Average	62.6	94.7	12.1	51.4	10.5	2.9	10.5	1.5	10.6	2.4	6.9	1	7	0.9	244.6	30.2	274.8
Min.	51	77.2	9.2	40.8	7.6	2.1	5.5	0.8	5.5	1.2	3.8	0.6	3.7	0.4	193.4	16	209.4
Max.	75.6	110.3	16.1	70.7	14.6	3.9	15.9	2.2	14.7	2.9	8.1	1.3	9.1	1.2	307.1	39.5	346.6
6W	65.5	73.8	9.7	38.6	8.1	2.9	10.3	1.6	16.8	2.9	8.3	1.6	10.8	1.3	208.9	43.3	252.2
7W	57.7	95.6	11.4	48.5	10.2	2.8	12.3	1.7	11.6	2.6	8.1	1.3	8.3	0.9	238.5	34.5	273
8W	50.9	108.6	10.8	41.3	8.4	2.2	7.5	1.3	8.1	1.9	5.4	0.8	6.7	0.7	229.7	24.8	254.5
9W	56.8	91.5	12.2	58.9	14.5	4.6	13.4	2	14.5	3.6	9.3	1.7	11.9	1.3	251.8	44.3	296.1
10W	39.9	62.4	7.5	29.3	5.8	1.6	6.4	1	6.7	1.5	4.6	0.7	4.6	0.5	152.9	19.5	172.4
Average	54.2	86.4	10.3	43.3	9.4	2.8	10	1.5	11.5	2.5	7.1	1.2	8.4	0.9	216.4	33.3	249.6
Min.	39.9	62.4	7.5	29.3	5.8	1.6	6.4	1	6.7	1.5	4.6	0.7	4.6	0.5	152.9	19.5	172.4
Max.	65.5	108.6	12.2	58.9	14.5	4.6	13.4	2	16.8	3.6	9.3	1.7	11.9	1.3	277.6	46.6	324.2
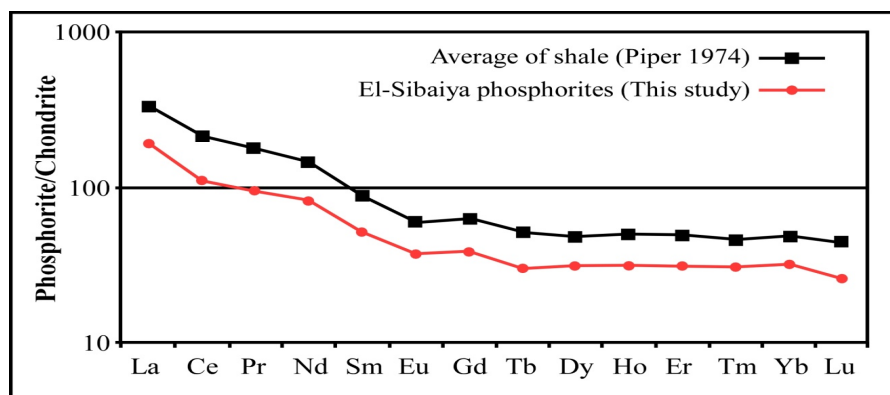
Fig.14: Chondrite normalized pattern of REEs from El-Sibaiya phosphorites with world average of shale (Piper,1974).

phoriteswith the world average shale (Piper 1974) that normalized to the chondrite REEs concentrations (Nakamura, 1974) can declare that:

The pattern exhibitsthe LREE's enrichment relative to the HREE's and slight negative Ce and Eu anomalies. The LREE's enrichment in the

1-Studied phosphorites may reflect post depositional modification of the REE's distribution in these deposits (Baioumy, 2011). The slight negative Ce and Eu anomalies can reveale their marine origin as well as the prevailing reducing conditions during their formation.

2-The pattern of the studied phosphorites is

in relative harmony with that of world average of shale. This may suggest that the REE's were derived from the associated clastic debris by diagenetic   remobilization as mentioned by (McArthur and Walsh 1985).

Laser ablation ICPMS

Ten composite phosphorite samples (five samples from each side) were analyzed using the ICPMS laser ablation. Ten spots were taken in every sample exactly in collophane pellets to cover their chemical composition (Fig.15).

The data obtained from the laser ablation technique (Table 6) can be used to illustrate the role of apatite mineral in the adsorption and accumulation of most of some elements which reflect the geochemical characteristic and peculiarities of the whole rock, where they show various elemental concentrations that mainly depend on their location either inside or outside the apatite lattice.

Some major elements especially Ca and F occur in high concentrations where they mostly locate within the apatite lattice and reveale positive correlation with phosphorus. On the other hand, Fe, Mg, Si, Al, Na, K and Ti are recorded in low concentrations which indicate that these elements locate outside the apatite lattice, as they have a negative correlation with P_2O_5.

Some trace elements also vary in their concentrations, where Cr, Zn, Ba, Sr and V are occurred in high content, whereas Ni, Cu, Zr, Rb and Y show lower content (Table 6).

The analyzed apatite minerals revealed higher concentration of REEs relative to the non-phosphatic minerals.

RADIOACTIVITY

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 (Adams et al., 1959 and Finch et al., 1973). In the present work, uranium and thorium contents within the studied phosphorites samples along the both sides of the Nile Valley were radiometrically measured and listed in Table (7).

The uranium content in El-Sibaiya East phosphorites ranges from 55.0 to 100.0 ppm with an average value of 81.6 ppm, while thorium content in these samples attains values between 1.0 to 7.0 ppm, with an average value of 3.1 ppm (Table 7).

On the other hand, the uranium content in El-Sibaiya West phosphorites ranges from
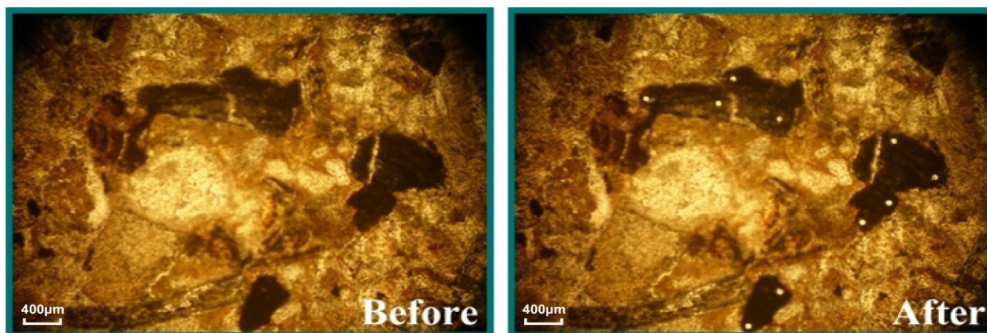

Fig.15: photomicrograph   showing   the   effect of laser ablation technique on pellets of collophane, El-Sibaiya phosphorites (XPL)

Table 6: Average complete chemical analyses using laser ablation ICPMS

| | Std. apatite | | 6E | E7 | E8 | E9 | E10 | W6 | W7 | W8 | W9 | W10 | Average |
	Duango1	Durango2											
Na	1404	1520	6935	5634	5603	5400	4099	40464	7961	28175	183404	4359	29203
Mg	157	164	1634	1281	1535	4336	1613	51796	2122	37768	47815	1258	15116
Al	4.57	6.11	1937	1063	1461	6475	236	190331	741	74667	3103	251	28026
Si	1607	1641	4427	3858	3399	20153	2306	1036453	2702	939870	950746	2312	296623
P	257235	272372	319625	357997	217303	206650	243551	230063	275158	197456	231557	176637	245600
K	34.5	16.8	743	930	698	1517	121	12180	525	21366	16318	501	5490
Ca	336910	336910	336910	336910	336910	336910	336910	336910	336910	336910	336910	336910	336910
Sc	1.02	0.69	8.86	9.96	15.1	23	6.24	91	21.4	59	10.9	9.51	25.5
Ti	4.11	5.14	130	131	193	427	84.9	4123	117	3827	88.7	50.3	917
V	32.6	34.4	526	142	459	1507	437	10870	61.3	2222	95.4	50.2	1637
Cr	16.5	7.33	208	93.22	287	502	118	80288	942	5507	142	93.8	8818
Mn	82.5	83.7	1918	1737	1222	2702	1721	9438	2201	20303	1426	1350	4402
Fe	343	380	93754	104531	213711	994328	92862	231607	34489	935864	46245	184016	293141
Co	0.26	0.21	6.81	7.34	5.93	35	2.77	149	6.48	436	3.45	4.77	65.8
Ni	0.53	0.49	162	43.4	122	915	50.7	1926	30.7	2517	27.5	23.5	582
Cu	0.64	0.66	78.2	25.8	64.2	218	39.2	525	26.2	1099	15.3	26	212
Zn	1.14	1.04	1478	158	1121	11970	812	25877	120	16259	328	44.2	5817
Ga	0.6	0.67	9.33	28.5	9.83	31.4	25.1	71.1	43.2	65.8	30.7	19.5	33.4
Ge	26.6	26.5	3.3	2.18	3.35	27.7	2.08	71.4	4.03	81.2	2.21	2.22	20
As	882	889	170	48.3	116	602	44.3	1574	31.5	1359	1342	34.2	532
Rb	0.12	0.11	0.9	3.84	1.19	7.09	0.16	40.2	1.63	16	92	0.47	16.3
Sr	439	449	1597	2117	1264	1960	2252	1802	2637	1215	1797	1711	1835
Y	672	702	55.8	110	89.3	267	29.1	45.8	226	68.7	138	60.2	109
Zr	2.66	1.84	28.1	27.1	23.6	65.7	14.4	490	17.7	151	306	16.4	114
Nb	0.05	0.06	0.39	0.29	0.45	1.35	0.29	9.6	0.41	5.98	0.2	0.12	1.91
Ag	0.82	<0.92	<1.90	1.19	0.69	<4.73	<0.49	9.77	0.83	4.71	7.08	1.14	3.63
Sn	0.11	0.13	1.67	0.32	0.72	9.22	0.44	72.1	0.56	17.7	0.74	0.15	10.4
Cs	0.02	0.03	0.03	0.23	0.16	0.49	0.02	7.07	0.12	0.62	1.71	0.06	1.05
Ba	1.64	1.62	103	476	141	439	447	423	642	580	696	375	432
La	3105	3171	30.3	56.5	51	219	16.3	27.3	127	50.9	37.9	39.9	65.6
Ce	4377	4788	49	77.2	86.4	463	24.1	30.8	211	109	61	62.4	117
Pr	367	384	5.78	9.21	9.93	52.8	2.75	4.05	25.9	10.8	8.1	7.51	13.7
Nd	1175	1172	23.5	40.8	41.8	233	11.6	16.1	107	41.3	39.3	29.3	58.4
Sm	166	172	4.92	7.55	8.46	48.1	2.48	3.38	22.4	8.37	9.69	5.76	12.1
Eu	13.6	14.6	1.34	2.12	2.47	13	0.69	1.22	6.31	2.24	3.09	1.58	3.41
Gd	148	151	5.49	10.1	10.4	52.7	2.66	4.3	27.1	7.46	13.4	6.4	14
Tb	19.5	20	0.84	1.46	1.47	7.22	0.41	0.68	3.9	1.29	2.01	0.97	2.03
Dy	115	120	5.53	10.9	10.4	48.5	2.89	7	25.4	8.08	14.5	6.71	14
Ho	23.4	23	1.19	2.74	2.39	9.8	0.68	1.23	5.9	1.94	3.6	1.48	3.1
Er	63.7	64	3.82	8.51	7.23	28.6	2.22	3.64	17.4	5.35	11.7	4.76	9.32
Tm	8.11	8.16	0.56	1.14	1.01	4.01	0.33	0.8	2.57	0.79	1.73	0.67	1.36
Yb	44.8	45.9	3.67	7.71	7.04	24.2	2.31	4.51	18.2	6.66	11.9	4.59	9.08
Lu	5.25	5.36	0.59	1.3	1.09	3.66	0.43	0.71	2.61	1.41	1.88	0.76	1.44
Hf	0.09	0.05	0.45	0.24	0.26	0.81	0.18	9.27	0.21	3.59	11.8	0.16	2.7
Ta	0.03	0.02	0.04	0.03	0.08	0.1	0.01	1.34	0.06	0.14	0.4	0.02	0.22
Au	0.04	0.03	0.15	0.02	0.03	<0.049	<0.0244	0.02	<0.027	0.2	0.02	<0.0214	0.07
Pb	0.82	0.91	9.5	22.2	9.36	33	6.89	195	21.6	248	6.44	8.81	56.1
Th	226	230	0.93	0.44	1.03	3.24	0.29	1.12	2.19	2.09	1.45	0.67	1.35
U	11.2	10.8	58.3	55.1	60.5	96.6	41.4	292.5	37.1	124.4	42.7	50.2	85.9

Table 7: Equivalent uranium contents (eU), equivalent thorium contents (eTh) and radium contents (Ra)

	eU (ppm)	eTh (ppm)	Ra (ppm)	eTh/eU	eU/eTh
6E	55.0	2.0	70.0	0.0	27.5
7E	97.0	7.0	105.0	uld	13.9
8E	87.0	3.0	97.0	uld	29.0
9E	95.0	1.0	90.0	uld	95.0
10E	58.0	1.0	67.0	uld	58.0
6W	72.0	5.0	63.0	0.1	14.4
7W	59.0	1.0	57.0	0.0	59.0
8W	45.0	3.0	52.0	0.1	15.0
9W	30.0	2.0	40.0	0.1	15.0
10W	73.0	3.0	68.0	0.0	24.3

E = Eastern side   W = Western side

30.0 to 73.0 ppm with an average value of 51.1 ppm, while the amount of thorium varies between 1.0 to 5.0 ppm, with an average value of 2.6ppm (Table 7).

Uranium / Element Relationships

In the present work, uranium content in the   studied area shows positive variations with P_2O_5, CaO and Sr with the correlation coefficient (r) 0.71, 0.70 and 0.51, respectively for El-SibaiyaEast and (r) 0.63, 0.52 and 0.51 respectively for El-Sibaiya West. On the other hand, it shows negative relationships with Fe_2O_3, SiO_2 and Ni with correlation coefficient (r) -0.56, -0.84 and -0.50 respectively for El-Sibaiya East and (r) -0.74 and -0.54 respectively for El-Sibaiya West (Figs. 16-19).

The positive correlation between U and P_2O_5, CaO and Sr reflects the role of apatite in the accumulation of U within the studied phosphorites. Also, this confirmed by the obtained results of laser ablation technique. These results are agreed with that of McKelvey and Carswell (1956). On the contrary, the negative correlation between U and Fe_2O_3 reflects that iron do not represent any role in

adsorption of uranium and/or this may be post depositional leaching processes of uranium from the iron minerals.

DISCUSSION

Cheney et al. (1979) recognized that the phosphatic deposits have a higher CaO/P_2O_5 ratio than that in the pure fluorapatite, where as the CaO in the francolite-type apatite remains nearly constant, whereas the P_2O_5 varies with the   substitution of carbonate and fluoride from 1.32 in pure fluorapatite to 1.62 in highly substituted francolite.

CaO/P_2O_5 ratio for the studied phosphorites 1.59; this relatively high ratio can refer to the presence of free carbonates and possibly to some non-phosphatic minerals such as gypsum or any clay fraction.

Some of the studied phosphorites exhibit F/P_2O_5 ratio reaches about 0.09. This ratio is close to the ideal one (0.089) recorded by Rooney and Kerr (1967) for pure fluorapatite. The apparent excess of F/P_2O_5 in some samples can be directly governed by the structural CO_2 content, owing to the replacement of PO_4 by $CO_3 + F$ (McArthur, 1985), or both
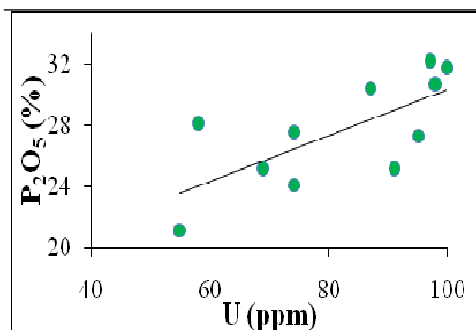
Fig.19: Correlation between uranium and SiO_2 (%) in the studied area
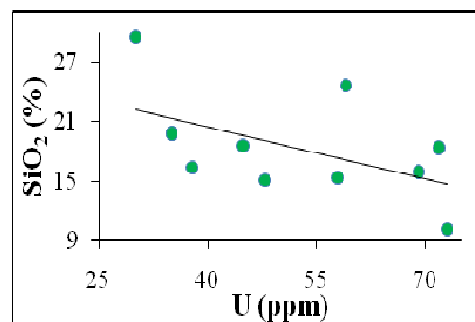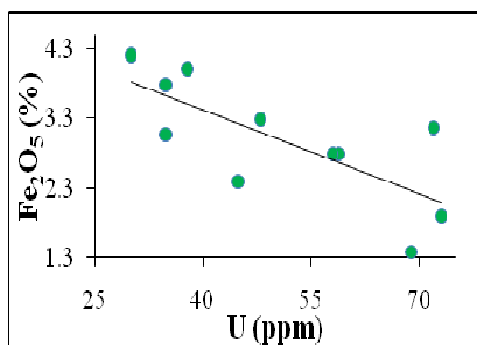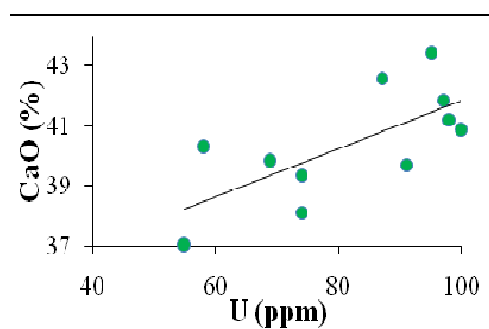

Fig.18: Correlation between uranium and CaO(%) in the studied area

CO_3 and $CO_3 + F$ (McClellan and Lehr, 1969). Minor fluorine may be associated with the organic matter and other constituents (Price and Calvert, 1978).

Iron in these deposits as elicited in the petrography present in the form of hematite, goethite and/or pyrite. Cook (1972) reported that iron can introduce into the apatite lattice by weathering.

McConnell (1973) believes that Si^{+4} may occur in the apatite structure as a substitution for phosphorus. Sharafeldine (1999) reported that the SiO_2 content in the bulk Egyptian phosphorite rocks reaches up to 15.40%, which is higher than those in the phosphatic pellets (2.17%).

Aluminum is reported by Cook (1972) as a major element tied primarily to the detrital contaminates in phosphorites located outside the apatite lattice.

Sodium content in the Egyptian phosphorites is mainly related to the presence of the halite mineral (Lehr et al. 1967).

Soliman et al. (2006) concluded that the elements V, Cr, Ni, Zn, Mo and Cu in phosphatic-rich shale are more enriched in clay fractions, organic matter and sulfides than in phosphatic components.

Garver and Royce (1993) suggested that where Cr and Ni concentrations are anomalously high, Cr/Ni ratio from 1.2 to 1.6 should be expected if these elements were derived from ultramafic rocks. Higher ratios are probably indicative of derivation from mafic volcanic rocks.

Copper is mainly associated with organic matter, where it has a high affinity to humic materials (Mohamed, 1979).

Mudroch (1983) reported that Cu and some other trace elements are commonly associated with the clay and silt size sediments as well as sulfides.

Zinc content can be compared with the world average (195 ppm) mentioned by Altschuler (1980) who concluded that the high content of Zn is attributed to the sulphate phase admixed in phosphorites.

Tooms et al. (1969) stated that Zr concentration in phosphorites may be governed by the ability of apatite lattice to assimilate it.

Pacey (1984) attributed the impoverishment of Zr in some phosphorites to its occurrence in extraneous detrital phases substituting for Ti in titaniferous minerals such as ilmenite.

Arrhenius (1963) mentioned that Ba occurs in the lattice of pelagic fish bone apatite. El-Kammar (1970) reported a positive correlation between Ba and Al in the Nile Valley phosphoritesand attributed this to its partial association with the clay fraction.

Strotium content is extremely higher than the world average (70 ppm) in phosphorites mentioned by Altschuler (1980), who also stated that Sr, Ba and Zn reveal a marked affinity towards fixation in the apatite crystal lattice.

Dabous (1981) attributed the strong positive correlation between P_2O_5 and CaO in the Nile Valley phosphorites to the presence of calcitic materials as cementing material.

The substitution of some elements in the apatite structure is reported by several authors especially McConnell (1952), Gulbrandsen (1966), Cook (1972) and Prevot and Lucas (1980). These authors recognized that V substitutes easily P as vanadate and occasionally reaching commercial concentration. Nickel behaves like V in the studied deposits, but its incorporation into apatite seems unlikely, which may illustrate its lower content in the present phosphorites. The analyzed samples show high values of Ba which positively correlates with CaO and P_2O_5. In spite of the larger ionic radius of Ba^{2+} relative Ca^{2+}, it may be accommodated within the carbonate fluorapatite lattice.

Also, the organic materials play a major role in the adsorption and accumulation of most of these trace elements within the studied phosphorites. According to Gulbrandsen (1966) and Mohamed (1979) Ni, Cr, V and Zn are thought to be associated with organic matter. The enrichment of some trace elements in phosphorites may be due to the reduction conditions induced by the organic matter (Toom et al., 1969).

Rare earth elements (REEs) concentrations with their characteristic patterns and Ce and Eu anomalies in marine phosphorites are useful indicators of marine depositional environments (Jarvis et al., 1994). Phosphorites commonly display highly variable REEs patterns due to the variations in the composition and amount of associated detritus, depositional environment, sea- and pore-water redox, pH, age and water depth (Picard et al., 2002). El-Kammar et al. (1979) cited that, REEs content of the Nile Valley phosphorites reflects the terrigeneous supply of the depositional sea rather than its depth.

Soliman (2003) reported that the concentration of REEs in phosphorites are related to some types of their components (fish debris).

Germann et al. (1987) confirmed the relative REEs enrichment of Abu Tartur phosphorites in the Western Desert compared to the Nile Valley and Red Sea regions.

From the radioactive view point, the stud-

ied phosphorites are characterized by uranium enrichment due to its long exposure to sea water and the capture of uranium in the apatite lattice.

CONCLUSIONS

The studied phosphorites show positive correlation between P_2O_5 and other elements that located inside the apatite lattice such as CaO, F and Sr, whereas P_2O_5 shows negative correlation with other elements that located outside the apatite lattice such as Fe_2O_3, SiO_2 and Al_2O_3.

P_2O_5 shows positive correlation with some trace elements such as Cr, Sr and V, reflecting the substitution of these elements within apatite.

Chondrite-normalized patterns of REEs against average shale show that, there is a strong coherence in the REEs distribution of the studied phosphorite and the REEs derived from the associated clastic debris by diagenetic remobilization. The patterns also show a marked LREEs enrichment relative to HREEs. The pronounced negative Ce-anomaly all over the studied samples emphasizes the marine character of the environment within which the phosphatic sedimentation or may due to post-depositional modifications.

Laser ablation analyses declared the major role of substitution processes in the enrichment of some elements such as Ca, F, Cr, Zn, Ba, Sr, V and REEs within apatite lattice. The concentration of the REEs within apatite particles confirmed the positive correlation between these elements and P_2O_5.

The uranium content in El-Sibaiya East phosphorites ranges from 55 to 100ppm with an average value of 81.6ppm, while in El-Sibaiya West phosphorites range from 30 to 73 ppm with an average value of 51.1 ppm. Apatite minerals play an important role in the accumulation of U within the studied phosphorites.

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إسهامات فى جيوكميائية فوسفات السباعية، وادى النيل، مصر

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يعتبر فوسفات السباعية، وادى النيل جزء من الحزام الرئيسي الممتد من الشرق الأوسط وشمال أفريقيا، يتواجد فوسفات الدراسة فى متكون الضوي وتقع منطقة الدراسة بين إدفو وقنا وذلك على كلا الجانبين من نهر النيل (السباعية شرق والسباعية غرب).

أوضحت التحاليل الجيوكيميائية أن عناصر الفوسفور والكالسيوم والفلور والصوديوم والماغنسيوم والاسترانشيوم هم المكونات الأساسية للصخور الفوسفاتية. أما بالنسبة لعناصر الألومنيوم والسيلكون والبوتاسيوم والحديد و التيتانيوم فيرتبط وجودها بالمعادن الطينية المصاحبة للخامات الفوسفاتية. كم أظهرت وجود علاقات طردية بين عنصر الفسفور وعناصر الكالسيوم، الفلور والاسترانشيوم. بينما تربطه علاقات عكسية مع عناصر الحديد، السيليكون والألومنيوم.

العناصر الأرضية النادرة تتواجد فى صخور الدراسة بمتوسط قدره ٢٦٢ جزء فى المليون وتمثل العناصر الأرضية النادرة الخفيفة نسبة ٨٥٪ بينما العناصر الأرضية النادرة الثقيلة ١٥٪. مع العلم بأن تواجد العناصر الأرضية النادرة بصخور الدراسة ليس فقط أثناء التكوين بل أيضا خلال العمليات اللاحقة

تم دراسة معادن الأباتيت باستخدام تقنية التزرية بواسطة الليز (الميكروبروب) وأظهرت الدراسة تنوع فى تركيزات العناصر طبقا لمكان تواجدها داخل أم خارج التركيب البلورى لمعادن الأباتيت. ويمكن القول بأن معادن الأباتيت غنية بعناصر الكالسيوم، الفلور، الكروميوم، الزنك، الباريوم، الاسترانشيوم، الفناديوم، والعناصر الأرضية النادرة مما يظهر دور معادن الأباتيت فى عمليات الاحلال وتركيز العناصر داخل تركيبها البلورى.

أثبتت الدراسة الإشعاعية أن الخامات الفوسفاتية بمنطقة الدراسة تتميز بتواجد العناصر المشعة مثل اليورانيوم والثوريوم نظرا لتعرضها الطويل لمياه البحر وزيادة تركيز اليورايوم فى البناء البلورى لمعادن الأباتيت.

يتراوح تركيز اليورايوم فى فوسفات السباعية شرق بين ٥٥ إلى ١٠٠ جزء من المليون بمتوسط قدره ٨١,٦ جزء من المليون. بينما فى السباعية غرب ٣٠ إلى ٧٣ جزء من المليون بمتوسط قدره ٥١,١ جزء من المليون.

تربط عنصر اليورانيوم علاقات طردية مع بعض العناصر أهمها الفسفور، الكالسيوم والاسترانشيوم. بينما تربطه علاقات عكسية ببعض العناصر منها الحديد، السيليكون والنيكل.