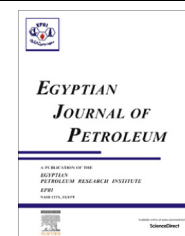




Egyptian Petroleum Research Institute  
**Egyptian Journal of Petroleum**

[www.elsevier.com/locate/egyjp](http://www.elsevier.com/locate/egyjp)  
[www.sciencedirect.com](http://www.sciencedirect.com)



FULL LENGTH ARTICLE

# Mineralogical, geochemical characteristics and origin of Late Cretaceous phosphorite in Duwi Formation (Geble Duwi Mine), Red Sea region, Egypt

Esmat A. Abou El-Anwar <sup>a,\*</sup>, H.S. Mekky <sup>a</sup>, S.H. Abd El Rahim <sup>a</sup>, S.K. Aita <sup>b</sup>

<sup>a</sup> Geological Sciences Dept., National Research Centre, Dokki, Giza, Egypt

<sup>b</sup> Nuclear Materials Authority, Cairo, Egypt

Received 15 November 2015; revised 10 January 2016; accepted 20 January 2016

## KEYWORDS

Mineralogy;  
 Geochemistry;  
 Duwi formation;  
 Phosphate;  
 REEs

**Abstract** The Late Cretaceous Duwi Formation in Egypt overlies non-marine, varicolored shale of the middle Campanian Quseir Formation. It is conformably overlain by gray, laminated, foraminiferal-rich marine shale of the middle Maastrichtian Dakhla Formation. Detailed mineralogical and geochemical studies were carried out on the phosphate rocks of the Duwi Formation in Quseir-Safaga province (Geble Duwi Mine) to infer their source rocks, paleo-weathering and provenance of the sources. The importance of the effect of phosphate rock depends on the chemical form of phosphorus in which this element is combined. This information is important in the assessment of possible radiological hazards to human health; due to the presence of uranium in the apatite structure. The phosphatic rock materials may be used as building stones or as phosphatic fertilizers and animal feed ingredients. Mineralogically, they are composed mainly of apatite (fluor-apatite), calcite and quartz with minor amounts of pyrite. The studied Duwi phosphates are authigenic in origin, comparable to those of phosphatic nodules of Peru and Chile margins. They are most probably derived from pre-existing authigenic phosphorites. Provenance, they originate from reworked older sedimentary phosphorites and biogenic sources. The geochemical data, CIA values suggested that the Duwi Formation phosphates were subjected to low chemical weathering.

Generally, the enrichment of the trace elements, REEs and uranium may have occurred during diagenesis. The studied phosphate samples were compared to the average of the Average World Phosphorite (AWP) and the Average Shale Composition (ASC). The major, trace and rare earth elements contents are compared with those in Egypt, North African, Asian and other localities. The ratios V/Cr, V/(V + Ni) and Mo/Al and the high concentrations of the redox sensitive elements revealed that the studied phosphates were deposited under anoxic reducing marine environments coupled with hydrothermal solutions, which is comparable to the environmental condition of

\* Corresponding author at: 33 El Buhouth St., Dokki, Cairo 12311, Egypt. Mobile: +20 1065497316; fax: +20 233387681. E-mail address: [abouelanwar2004@yahoo.com](mailto:abouelanwar2004@yahoo.com) (E.A. Abou El-Anwar).

Peer review under responsibility of Egyptian Petroleum Research Institute.

<http://dx.doi.org/10.1016/j.ejpe.2016.01.004>

1110-0621 © 2016 Egyptian Petroleum Research Institute. Production and hosting by Elsevier B.V.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

the associated black shales. The concentration of the trace and toxic elements in the studied samples are considered to be below the limits for most field-grown crops.

© 2016 Egyptian Petroleum Research Institute. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Composition of the phosphate rocks mostly depends on their type and origin. About 90% rocks are used in the production of P-fertilizers and the remains 10% is used as a source of phosphorous for chemical and food industries [1]. Phosphate resources are distributed, according to their type, approximately as follows: 75% from sedimentary marine deposits, 15–20% from igneous, metamorphic and weathered deposits, and 2–3% from biogenic sources (bird and bat guano accumulations) [2]. Its current abundance in the earth's crust is approximately 0.12%; and almost all of the phosphorus on earth is found in the form of minerals including chloro and fluoro-apatite, vivianite, wavellite, and phosphorites [3,4].

Sedimentary rocks contain high concentrations of heavy metals. These deposits occur in the form of ore bodies or lenses in one thick bed or several beds intercalated with sedimentary non-phosphate materials. Sedimentary phosphate ores show a wide diversity in the composition of their gangue materials, but generally fall into one of the three categories: siliceous, clayey and calcareous ores. It is known that most sedimentary calcareous phosphate rocks contain considerable quantities of carbonates and are considered to be carbonate-apatite or francolites. Because of the increasing use of phosphate in industry worldwide, it is interesting to investigate the elemental concentration in phosphate ores. The trace element content of certain phosphate rocks is critical for their utilization and consequently, determination of the concentration of Ni, Zn, and U (environmental pollutants i.e. toxic elements), and the common elements (Co, K, Mg, Mn, Na) in phosphate rocks used for the production of fertilizers in Egypt.

In the present study the authors focus on the geochemical composition of phosphates of the Duwi Formation, in an effort to recognize its provenance, source weathering history, and the depositional environment. These factors are evaluated using major oxides, trace, and rare earth element (REEs) data, weathering indices, elemental ratios, and other geochemical indicators.

## 2. Geological setting

Most of the known world phosphate rock reserves are found in sedimentary marine deposits of the Upper Cretaceous and Eocene ages of the Mediterranean phosphogenic province; which exist in Morocco, Spain, Sahara, Algeria, Tunisia, Egypt, Israel, Jordan, Syria, Saudi Arabia, Turkey and Iraq. They are made of deposits laid down in the ancient Tethys Sea of the Mesozoic and Tertiary ages. The importance of the phosphate rock deposits in the Upper Cretaceous and Eocene ages is that they form more than 70% of the total world phosphate reserves [5,6].

Phosphorite deposits in Egypt, known as the Duwi Formation, are a part of the Middle East to North Africa phosphogenic province of Late Cretaceous to Paleogene age. They

are found in: the Nile Valley, between Idfu and Wadi Qena, the Red Sea Coast, between Safaga and Quseir, Abu Tartur plateau in Western Desert and Sinai. These deposits belong to the Duwi Formation and its equivalent formations of Campanian–Maastrichtian age. The Duwi Formation in the Red Sea, Nile Valley, and Abu-Tartur areas overlies non-marine, varicolored shale of the middle Campanian Quseir Formation, and is conformably overlain by gray, laminated foraminifer-rich marine shale of the middle Maastrichtian Dakhla Formation [7]. These sediments are reflecting deposition under inner neritic to outer shelf conditions and repeated sea level changes [8]. Abd El-Gabar et al. [9] reveal the presence of uranium phosphate mineral phosphuranylite, belovite and phosphoferite in all phosphate rocks in the Red Sea, Nile Valley and Western Desert. Moreover, they indicated that the uranium contents increase as  $P_2O_5$  exceeds 15% with an average of 107 ppm. These values drop to an average of 36 ppm with  $P_2O_5$  less than 15%. Individual phosphorite beds in the Duwi Formation range in thickness from a few millimeters to tens of centimeters. One common feature of nearly all Duwi phosphorites is the extensive bioturbation. As a result, most of the phosphate beds appear massive and internally structureless.

Quseir-Safaga areas are part of the Eastern Desert of Egypt at the Red Sea Coast, and gained importance since the phosphate deposits of the Gebel Duwi Range were discovered and exploited. The region extends in a northwest direction along the western coast of the Red Sea from south of Quseir to Safaga, between Longitudes  $33^{\circ}45'–34^{\circ}25'$  E and Latitudes  $25^{\circ}50'–26^{\circ}67'$  N, covering an area of about 500 km<sup>2</sup>. Typically, the Egyptian phosphates are shallow marine deposits of Upper Cretaceous age. Their maximum intensity of deposition was associated with a transgressive shoreline of the Late Campanian or Early Maastrichtian Sea which encroached from north to south over the northern slope of Africa [10,11]. The chosen area is located at Longitudes  $34^{\circ}03'12''–34^{\circ}03'24''$  E and Latitudes  $26^{\circ}11'27''–26^{\circ}11'37''$  N (Figs. 1 and 2), [12,13].

## 3. Mineralogy

The mineralogical composition was identified using the X-ray technique with a Phillips X-ray diffractometer model and Ni-filtered  $Cu-K\alpha$  radiation at the Metallurgical Center for the Research and Development Institute (Tebbin, Egypt). The XRD analysis showed the dominance of apatite (fluorapatite) in the tested samples while the associated gangue minerals are calcite and quartz with minor amounts of pyrite. Apatite  $\{Ca_5(PO_4)_3[F, OH \text{ or } Cl]\}$  in most sedimentary calcareous phosphate rocks contains considerable quantities of carbonates and is considered to be carbonate-apatite or francolites. Many authors presented evidence that, as in a typical sedimentary ore in the Duwi Formation, its main phosphate mineral is francolite (carbonate fluorapatite). In addition, many accessory phosphate minerals were also reported in Abu-Tartur such as fluor-apatite, hydroxyapatite, dolomite, quartz,

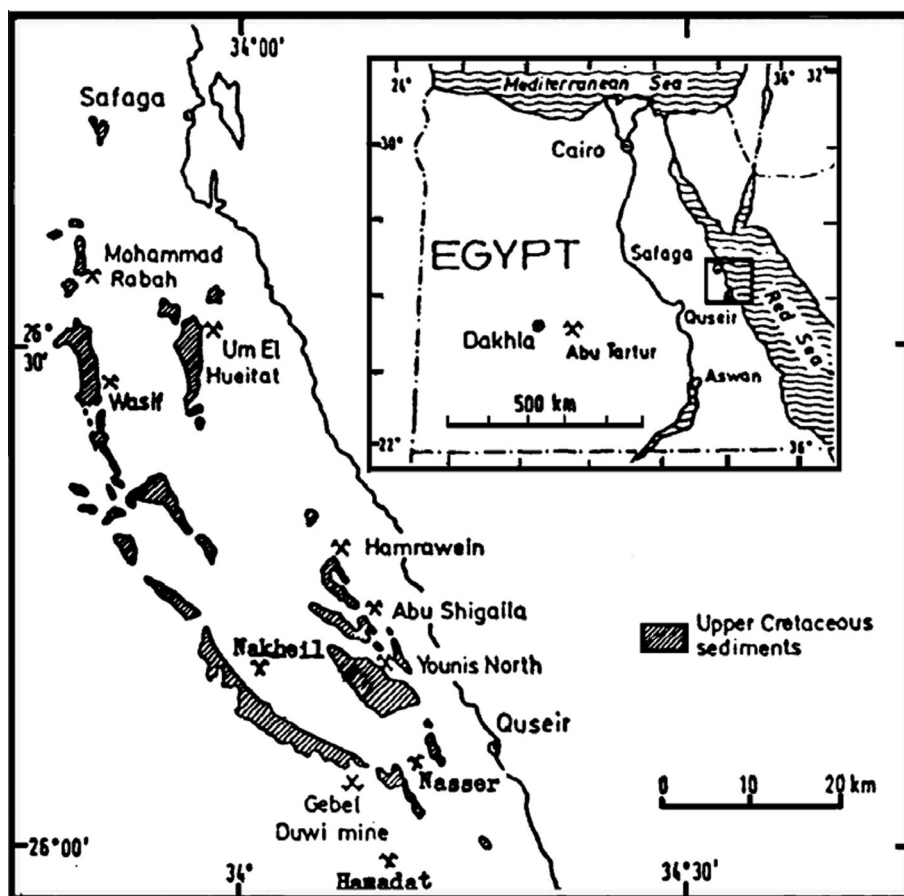


Figure 1 Location and geological maps for the studied area (after Ganz et al., 1987) [12].

gypsum, pyrite, aragonite, dehrnite, manganatite, glauconite, lewistonite, wilkeite, dahllite, and chlorapatite [14,3,15]. The presence of calcite in the studied samples and the forams tests from the petrographic study (in press) may reveal that the deposition of this phosphate was in highly agitated shallow marine environment; which is in agreement with that of Abou El-Anwar et al. [16].

#### 4. Chemical composition of phosphate rocks

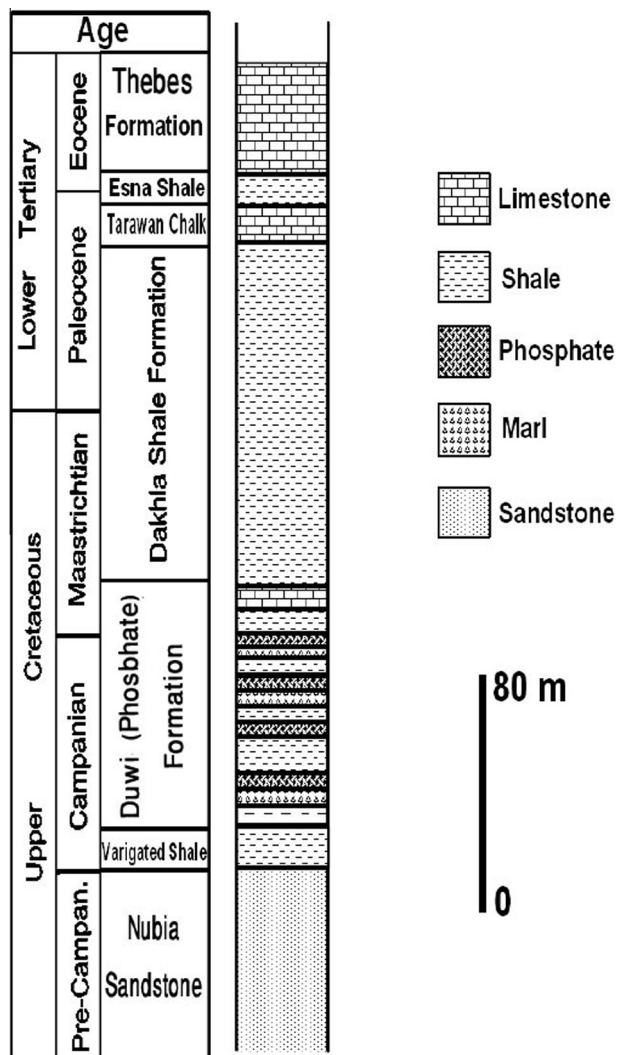
Geochemical distribution of certain major oxides and trace elements may provide direct information on the depositional environment. We obtained data of major oxides, trace and some rare earth elements (Table 1), for the studied selected phosphate samples using Axios Sequential WD\_XRD Spectrometer, Analytical 2005 in the National Research Center Laboratory.

All major oxides and trace elements show relative homogeneity in the composition.  $P_2O_5$  ranges from 25.01% to 25.9% with an average of 25.67% (Table 1). The value is higher than averages of phosphate of Red Sea region (16.43%, 23.65% and 19.3%) recorded by Abd El-Gabar et al. [9]; Baioumy and Tada [17] and El-Taher [3]; respectively, (Table 2 and Fig. 3). Also, it is higher than the average values of the Nile Valley given by Abdel-All and Amer [18]; Abd El-Gabar et al. [9] and Baioumy and Tada [17], but lower than the value mentioned by El Taher [3]. This present average is higher

than the average values of the Abu Tartur phosphates of Abd El-Gabar et al. [9] and Awadalla [15]; but comparable for that signed by Baioumy and Tada [17] as in Table 2 and Fig. 3. Phosphate ores are divided into three groups according to their  $P_2O_5$  content; low (12–16%  $P_2O_5$ ), intermediate (17–25%  $P_2O_5$ ), and high-grade ores (26–35%  $P_2O_5$ ). Accordingly, the studied phosphate belongs mainly to high grade [5,6,4]. Sr/ $P_2O_5$  ratios ranging from  $5.94 \times 10^{-3}$  to  $6.6 \times 10^{-3}$  (Table 1), these values are comparable to those obtained for other sedimentary phosphate rocks [19].

Fluorine ranges from 1.61% to 1.8%, averaging 1.7% (Table 1). Carbonate fluorapatite [ $Ca_5(PO_4, CO_3)_3(F)$ ] having more than 1% of fluorine. Meanwhile, the carbonate hydroxyapatite with a fluorine content which does not exceed 1% called dahllite [20], contain more than 20% of  $P_2O_5$ , and is composed of Ca-phosphate minerals of the apatite group, such as hydroxyl-fluorapatite [ $Ca_5(PO_4)_3(OH, F)$ ], carbonate fluorapatite [ $Ca_5(PO_4, CO_3)_3(F, OH)$ ], also called francolite, and a low crystalline to cryptocrystalline variety of francolite called cellophane [21]. Therefore, the composition of the studied phosphate is mainly fluorapatite; which is in agreement with the obtained XRD data. However, the relation of F with  $TiO_2$  ( $r = 0.93$ ), reflects that it may be associated with the heavy metals (Table 3).

CaO ranges in the studied samples from 54.95% to 59.11% and  $SiO_2$  ranges from 9.2% to 10.1%. The L.O.I. values range between 0.16% and 4.01%, with an average 1.98%. The lower



**Figure 2** Schematic section of the studied Gebel Duwi Mine (after Faris, 1982) [13].

averaging content of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$  (0.68%, 0.66% and 0.37%; respectively), indicates that the studied phosphates precipitated in sedimentary basins [21], which conformed with the  $\text{Sr}/\text{P}_2\text{O}_5$  ratios (Table 1). Ca and  $\text{P}_2\text{O}_5$  relation shows negative relation, ( $r = -0.72$ ) as a result of the presence of Ca mainly in the carbonates as calcite and in apatite (Table 3). This indicates the presence of calcite cement in phosphorite; a result of later diagenesis [22]. The high average silica content (9.63%) is an indication of biogenic origin [23]. The  $\text{CaO}/\text{P}_2\text{O}_5$  ratio of the studied phosphate shows an average of 2.22. The increase than the normative carbonate fluorapatite (1.58) may be due to either the substitution of  $\text{PO}_4$  by  $\text{CO}_3$  or the presence of calcite in the phosphorites (Table 1). The negative correlation between  $\text{SiO}_2$  and  $\text{P}_2\text{O}_5$  ( $r = -0.74$ ) is related to the detrital quartz. Quartz and calcite are detected by XRD in the studied phosphate rocks.  $\text{MgO}$  has a strong positive correlation with  $\text{P}_2\text{O}_5$  ( $r = 0.77$ ) which indicates that  $\text{Mg}^{2+}$  replaces  $\text{Ca}^{2+}$  in the phosphate mineral structures. The correlation coefficient between  $\text{Al}_2\text{O}_3$  versus  $\text{V}_2\text{O}_5$  and  $\text{TiO}_2$  ( $r = 0.83$  and 0.70; respectively), indicate enrichment of the immobile elements V and Ti during the chemical weathering condition.

The low  $\text{Fe}_2\text{O}_3$  content of the studied phosphate averaging (0.66%) indicate the formation of phosphate in the near-surface oxidizing environment [24]. The strong positive correlation between  $\text{Fe}_2\text{O}_3$  and  $\text{SrO}$  ( $r = 0.98$ ) indicates that iron oxy-hydroxides may scavenge and uptake Sr, which is an essential function of many microbes [25–29,16]. The strong negative correlation (Table 3) between  $\text{P}_2\text{O}_5$  with  $\text{Fe}_2\text{O}_3$  and Sr ( $r = -0.77$  and  $-0.65$ ; respectively) is possibly indicating that absence of belovite {phosphoferrite  $\{(\text{FeMn})_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}\}$  and  $\text{Sr}_3(\text{CeNaCa})_2(\text{PO}_4)_3\text{OH}\}$ , which is recorded in the phosphates of the Nile Valley and Abu Tartur [9].

Sulfur contents recorded 1.48% as an average, are comparable to the average value considered by Baioumy and Tada [17] for the Red Sea phosphorites (1.32%). However, it is lower than the Abu-Tartur and the Nile Valley phosphates values (average 4.73% and 2.02%; respectively), [17]. On the other hand, the strong positive relation between  $\text{SO}_3$  and  $\text{P}_2\text{O}_5$  ( $r = 0.82$ ) indicate that the S may be accompanied as bacterial action and later on as diagenetic process in the form of pyrite. Hence, the soil treatment with phosphate rock in combination with sulfur-oxidizing bacteria could be used to improve soil fertility for good quality and high yield of crop production [1,30–32]. The lower content of Al, Fe and Cl with P increases so the P can be adsorbed to the soil and decreases the risk of leaching [33,34].

La, Co, V and Zn recorded positive relations with  $\text{SiO}_2$  ( $r = 0.71, 0.64, 0.47$  and  $0.43$ ; respectively) Table 3. The trace and some rare earth elements in the studied area are generally associated with detrital minerals; those introduced by weathering and associated with organic matter and those located within the apatite lattice, which is in agreement with El-Kammar et al. [35] for Nile Valley phosphorites. Sm recorded positive relations with NiO, MgO and  $\text{SO}_3$  ( $r = 0.70, 0.61$  and  $0.64$ , respectively; Table 3). This indicated that Sm is associated with heavy metals and pyrite. The correlation between  $\text{Al}_2\text{O}_3$  and As ( $r = -0.45$ ) indicates probable detrital origin of As. The positive correlation between  $\text{P}_2\text{O}_5$  and As ( $r = 0.53$ ) suggests that there is genetic relationship between As and francolite. The positive correlation ( $r = 0.35$ ) between As and S suggests the occurrence of As as sulfide. This leads to the conclusion that the geochemistry of As is related to the post-depositional conditions (diagenesis) rather than the formational conditions of the studied Egyptian phosphorite grains. Generally, the trace and rare earth elements are higher than those reported values in the PAAS [36].

## 5. Depositional environments

According to the relative abundance of the trace elements with associated sediments, they can be classified into four main groups: (1) phosphate group (including Ba, Cr, Sr, U, V and Zn), (2) organic matter group (Be, Co, Cu, Mo and Ni), (3) clay fraction group (Pb and Mn), and (4) the detrital fraction group [37]. The studied samples are relatively high in the phosphate group elements such as Zn, V, Cr and Sr and organic matter group; and Co, Mo and Ni, and Mn as a clay fraction (Table 4). Enriched concentration of Cu, Co, Ni and Zn in the phosphorites has been considered to be typical of organic matter derived from marine plankton which is in agreement with the petrographic studied (in press). In contrast to Sr, Fe and Mn contents (Table 4), reflect more the redox state of the

**Table 1** Chemical analysis data of major oxides (%) and trace elements (ppm), CIA and elemental ratios of the studied phosphates.

Element	1	2	3	4	5	Min.	Max.	Average	Av. B. Sh
P <sub>2</sub> O <sub>5</sub>	25.88	25.01	25.75	25.9	25.8	25.01	25.9	25.67	3.42
SiO <sub>2</sub>	9.51	10.1	9.95	9.4	9.2	9.2	10.1	9.63	15.89
TiO <sub>2</sub>	0.04	0.05	0.04	0.05	0.04	0.04	0.05	0.04	0.33
Al <sub>2</sub> O <sub>3</sub>	0.67	0.73	0.7	0.6	0.7	0.6	0.73	0.68	5.29
Fe <sub>2</sub> O <sub>3</sub>	0.66	0.68	0.65	0.65	0.67	0.65	0.68	0.66	3.61
MnO	0.06	0.06	0.05	0.05	0.06	0.05	0.06	0.06	0.02
NiO	0.01	0	0.01	0.01	0.01	0	0.01	0.01	0.05
ZnO	0.02	0.02	0.03	0.02	0.02	0.02	0.03	0.02	0.15
MgO	0.39	0.36	0.37	0.38	0.37	0.36	0.39	0.37	0.64
CaO	55.36	59.11	57.64	54.95	58.4	54.95	59.11	57.09	21.4
Na <sub>2</sub> O	0.27	0.25	0.26	0.26	0.25	0.25	0.27	0.26	0.13
K <sub>2</sub> O	0.05	0.05	0.05	0.04	0.05	0.04	0.05	0.05	0.45
SO <sub>3</sub>	1.49	1.37	1.45	1.6	1.5	1.37	1.6	1.48	7.24
SrO	0.185	0.19	0.18	0.182	0.188	0.18	0.19	0.19	0.08
V <sub>2</sub> O <sub>5</sub>	0.04	0.05	0.05	0.04	0.05	0.04	0.05	0.05	0.44
Cl	0.07	0.06	0.07	0.06	0.07	0.06	0.07	0.07	0.03
As	23	0	45	30	0	0	45	19.60	17
Mo	350	421	200	320	326	200	421	323.40	647
Cr	90	109	87	320	201	87	320	161.40	739
Co	3	4.5	2	1.5	2	1.5	4.5	2.60	n.d.
F	1.61	1.77	1.69	1.8	1.65	1.61	1.8	1.70	0.25
La	34	62	25	23	22	22	62	33.20	n.d.
Sm	7	3	4	6	8	3	8	5.60	n.d.
U	75	20	40	80	35	20	80	35	n.d.
L.I.O	3.68	0.16	1.06	4.01	0.98	0.16	4.01	1.98	39.99
CaO/P <sub>2</sub> O <sub>5</sub>	2.14	2.36	2.24	2.12	2.26	2.12	2.36	2.22	6.26
V/Cr	2.34	2.39	3.19	0.67	1.34	0.67	3.19	1.99	3.22
V(V + Ni)	0.68	1.00	0.77	0.70	0.72	0.68	1.00	0.77	0.86
Ti/Al	0.06	0.07	0.06	0.08	0.06	0.06	0.08	0.07	0.06
K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	0.03	0.04	0.04	0.02	0.04	0.02	0.04	0.03	0.09
Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	16.75	14.60	17.50	12.00	17.50	12.00	17.50	15.67	16.04
MgO/Al <sub>2</sub> O <sub>3</sub>	0.582	0.49	0.53	0.63	0.53	0.493	0.633	0.55	0.12
K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	0.075	0.068	0.071	0.067	0.071	0.067	0.068	0.071	0.09
Sr/P <sub>2</sub> O <sub>5</sub>	6.07 × 10 <sup>-3</sup>	6.6 × 10 <sup>-3</sup>	5.94 × 10 <sup>-3</sup>	5.99 × 10 <sup>-3</sup>	6.16 × 10 <sup>-3</sup>	5.94 × 10 <sup>-3</sup>	6.6 × 10 <sup>-3</sup>	6.15 × 10 <sup>-3</sup>	
Moppm/Al%	985.6	1088.1	539.1	1006.3	878.7	539.1	1088.1	899.7	654.4
Cr/Ni	0.93	0	0.9	3.3	2.07	0	3.3	1.44	1.99
CIA	53.17	57.03	55.12	51.72	56	51.72	57.03	54.61	88.16

Note: CIA, Chemical Index of Alteration; n.d., not determined; Av. B. Sh., average black shales studied by Abou El-Anwar et al. [16].

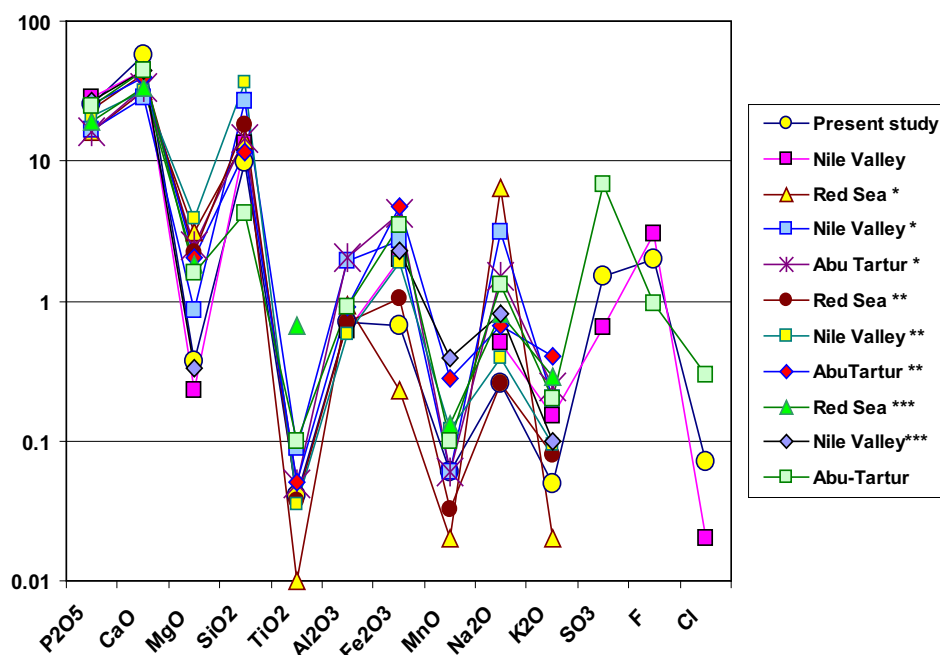
diagenetic environment [36,38,16]. The ratios V/Cr (1.99), V/(V + Ni) 0.77 and Mo/Al (899) are comparable to those of the associated black shales [16], Table 1. This revealed that the studied phosphatic rocks deposited under anoxic marine environments. The high contents of trace metals, such as Zn (149 ppm), indicate deposition in the anoxic basis of the water column. Molybdenum is a conservative element in the oxic marine environment [39]. The Mo/Al ratios in the studied samples range from 539.1 to 1088.1 (ppm/Al), with an average 899.7 (ppm/Al). This is obviously higher than the PAAS shale standard value [40]. This revealed that the Mo enrichment in the phosphatic rocks occurred under anoxic conditions, [41]. Such conditions can only result from anaerobic bacterial activity. The condition is relatively similar to the formation of the Sonrai phosphorites of India [42]. The variations in the trace element distribution during sediment diagenesis suggested that certain trace elements recycle back to the water column in oxic conditions and retain the sediments under anoxic conditions [43]. This indicates that planktonic organic matter may not alone be the main source of elements in the phosphatic rocks [44].

The trace elements V, Ni, Cr, Zn and Mo in the studied phosphate show averages of 246, 72, 161, 149 and 323 ppm; respectively, which is lower than those of the associated black shales (2331, 375, 739, 1230 and 647 ppm; respectively), studied by Abou El-Anwar et al. [16], Table 1. This indicates leaching processes outgoing from the overlain or underlined black shales [45,46]. The U contents of the collected phosphate samples range from 20 ppm up to 80 ppm with an average of 50 ppm. The U contents are positively correlated with the P<sub>2</sub>O<sub>5</sub> % contents ( $r = 0.75$ ), which indicate that the radioactive anomalies are mainly due to the presence of phosphatic components hosting uranium in their apatite structure. This also, reflects the effect of phosphate ion in the fixation of uranyl ion and the formation of secondary uranium phosphate minerals such as “phosphuranylite” comparable to that on the Red Sea Coast and Abu Tartur which are in agreement with Abd El-Gabar et al. and El-Kammar and El-Kammar [9,55]. Consequently, the liberation of uranium from the apatite lattices, as a result of intensive post-depositional diagenetic processes, led to the migration and disequilibrium state

**Table 2** Major oxide composition of the phosphates in this study is compared with published average for different localities in Egypt.

Major oxides%	Present study	Abdel. Alla & Amr [18]	Abd El-Gabar et al. [9]						Baioumy [17]			El Taher [3]			Awad Alla [15]
			Red Sea		Nile Vally		W. Desert	Red Sea	Nile Valley	Abu Tartur	Red Sea	Nile Valley	Abu-Tartur		
			G. Yunis	G.Um Ho.	W. Hamm.	G. El-Qam								El-Maham.	
P <sub>2</sub> O <sub>5</sub>	25.67	28.5	14.99	17.86	20.56	15.56	13.47	16.15	23.65	20.75	25.29	19.3	27.1	24.6	
CaO	57.37	44.6	28.67	35.57	30.85	25.14	30.02	33.42	41.66	31.86	39.25	33.16	44.36	43.8	
MgO	0.37	0.23	5.29	0.88	0.59	0.53	0.93	2.45	2.19	39	2.05	1.82	0.33	1.6	
SiO <sub>2</sub>	9.85	13.3	8.76	19.31	29.57	28.82	22.31	14.66	17.99	37.01	11.54	N.D.	N.D.	4.2	
TiO <sub>2</sub>	0.04	N.D.	0.01	0.01	0.11	0.11	0.06	0.05	0.037	0.035	0.051	0.67	N.D.	0.1	
Al <sub>2</sub> O <sub>3</sub>	0.7	0.62	0.8	1.04	1.18	2.64	2	2.06	0.7	0.58	0.91	N.D.	N.D.	0.9	
Fe <sub>2</sub> O <sub>3</sub>	0.66	2	0.31	0.14	1.36	4.66	2.03	4.17	1.045	1.9	4.73	ND	2.29	3.5	
MnO	0.06	N.D.	0.04	N.D.	0.05	0.11	0.01	0.06	0.032	0.12	0.28	0.132	0.39	0.1	
Na <sub>2</sub> O	0.26	0.5	8.42	4.53	1.6	3.31	4.54	1.52	0.26	0.39	0.66	0.81	0.81	1.3	
K <sub>2</sub> O	0.05	0.15	0.02	0.02	0.19	0.33	0.08	0.24	0.08	0.093	0.4	0.29	0.1	0.2	
SO <sub>3</sub>	1.48	0.65	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	6.9	
F	1.96	2.99	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.95	
Cl	0.07	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.3	

Note: N.D. = not determined.



**Figure 3** Major oxides of the phosphates in the study area as compared with published average phosphates. Nile Valley (Abdel-All and Amer, 1995) [18]; Red Sea\*, Nile Valley\* and Abu Tartur\* (Abd El-Gabar et al., 2002) [9]; Red Sea\*\*, Nile Valley\*\* and Abu Tartur\*\* (Baioumy, 2005) [17]; Red Sea\*\*\*, Nile Valley\*\*\* and Abu Tartur\*\*\* (El-Taher, 2010) [3] and Abu Tartur (Awad Alla, 2011) [15].

of the uranium content in the phosphorite beds, which is in agreement with Aita et al. [47].

The low average content of detrital terrigenous influx Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> and the association of the phosphate bed with oyster limestone in Quseir indicate the marine origin of the phosphates in the Eastern part of Egypt. Generally, the enrichment of trace elements and REEs may have occurred during diagenesis. Consequently, the studied phosphatic rocks deposited under anoxic marine conditions coupled with hydrothermal solutions which are similar to the associated black shales [16].

## 6. Source rocks

Fig. 4 shows the strong positive correlation ( $r^2 = 0.816$ ) between Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O in the studied phosphate. Meanwhile, this correlation is very weak in the associated shales ( $r^2 = 0.096$ ) probably revealing a change in source of the detrital influx. Table 1 shows the differences in Ti/Al and K/Al ratios between the studied phosphorites and the associated black shales calculated by Abou El-Anwar et al. [16]. It can be attributed to the difference in the source of detrital material

**Table 3** Correlation coefficients of the major oxides and trace elements in the studied phosphates.

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	NiO	ZnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	SrO	V <sub>2</sub> O <sub>5</sub>	Cl	As	Mo	Cr	Co	F	La	Sm	U	P <sub>2</sub> O <sub>5</sub>	L.I.O	
SiO <sub>2</sub>	1.00																									
TiO <sub>2</sub>	0.28	1.00																								
Al <sub>2</sub> O <sub>3</sub>	0.54	-0.28	1.00																							
Fe <sub>2</sub> O <sub>3</sub>	0.21	0.21	0.70	1.00																						
MnO	-0.10	-0.17	0.55	0.84	1.00																					
NiO	-0.69	-0.61	-0.56	-0.77	-0.41	1.00																				
ZnO	0.47	-0.41	0.23	-0.51	-0.61	0.25	1.00																			
MgO	-0.55	-0.32	-0.66	-0.57	-0.08	0.69	-0.20	1.00																		
CaO	0.45	-0.03	0.89	0.72	0.39	-0.61	0.17	-0.90	1.00																	
Na <sub>2</sub> O	-0.12	-0.33	-0.48	-0.64	-0.22	0.53	0.13	0.89	-0.82	1.00																
K <sub>2</sub> O	0.34	-0.61	0.90	0.51	0.61	-0.25	0.25	-0.29	0.65	-0.13	1.00															
SO <sub>3</sub>	-0.78	0.03	-0.93	-0.67	-0.47	0.75	-0.21	0.65	-0.79	0.37	-0.79	1.00														
SrO	0.02	0.22	0.55	0.98	0.89	-0.68	-0.68	-0.43	0.58	-0.58	0.41	-0.51	1.00													
V <sub>2</sub> O <sub>5</sub>	0.43	-0.17	0.83	0.49	0.17	-0.41	0.41	-0.88	0.96	-0.76	0.61	-0.69	0.33	1.00												
Cl	-0.28	-1.00	0.28	-0.21	0.17	0.61	0.41	0.32	0.03	0.33	0.61	-0.03	-0.22	0.17	1.00											
As	0.15	-0.21	-0.45	-0.93	-0.83	0.56	0.73	0.41	-0.55	0.65	-0.30	0.35	-0.98	-0.32	0.21	1.00										
Mo	0.02	0.54	0.16	0.78	0.73	-0.68	-0.86	-0.13	0.16	-0.28	0.02	-0.27	0.85	-0.13	-0.54	-0.81	1.00									
Cr	-0.61	0.48	-0.77	-0.29	-0.38	0.29	-0.42	0.15	-0.42	-0.17	-0.89	0.81	-0.15	-0.40	-0.48	-0.03	0.05	1.00								
Co	0.64	0.31	0.66	0.79	0.65	-0.89	-0.28	-0.40	0.50	-0.23	0.52	-0.83	0.71	0.27	-0.31	-0.54	0.71	-0.59	1.00							
F	0.32	0.93	-0.30	-0.01	-0.47	-0.46	-0.10	-0.43	0.02	-0.40	-0.67	0.10	-0.04	-0.01	-0.93	0.01	0.20	0.54	0.06	1.00						
La	0.71	0.51	0.56	0.74	0.50	-0.96	-0.27	-0.49	0.48	-0.30	0.34	-0.78	0.66	0.26	-0.51	-0.50	0.72	-0.45	0.97	0.29	1.00					
Sm	-0.96	-0.48	-0.39	-0.15	0.26	0.70	-0.43	0.61	-0.41	0.23	-0.11	0.64	0.03	-0.40	0.48	-0.17	-0.02	0.38	-0.54	-0.56	-0.66	1.00				
U	-0.52	0.00	-0.90	-0.69	-0.35	0.64	-0.21	0.92	-1.00	0.80	-0.64	0.82	-0.54	-0.96	0.00	0.50	-0.14	0.45	-0.52	-0.06	-0.51	0.48	1.00			
P <sub>2</sub> O <sub>5</sub>	-0.74	-0.52	-0.67	-0.77	-0.38	0.99	0.12	0.77	-0.72	0.59	-0.35	0.82	-0.65	-0.54	0.52	0.53	-0.58	0.37	-0.87	-0.41	-0.93	0.74	0.75	1.00		
L.I.O	-0.53	0.06	-0.89	-0.63	-0.29	0.58	-0.29	0.91	-0.99	0.77	-0.65	0.80	-0.47	-0.98	-0.06	0.43	-0.05	0.46	-0.46	-0.03	-0.45	0.48	1.00	0.70	1	

**Table 4** Trace elemental composition of the phosphates in this study are compared with published average for different localities in Egypt.

Element ppm	Present study	El-Kammar and El-Kammar [55]				El Taher [3]		Awad Alla [15]
		Red Sea	Nile Valley	Abu Tartur	Sinia	Red Sea	Nile Valley	Abu Tartur
Ni	77	ND	ND	ND	ND	469	22	ND
Zn	149	171	119.7	86.3	106.2	360	162	133
Sr	1705	1350	1385	1584	391	520	1032	1001
V	246	ND	ND	ND	ND	ND	220	30
Cr	161.4	95	77.6	56.63	59.6	ND	ND	200
Co	2.6	3.2	6.55	37.22	2.12	ND	ND	ND
Mo	323.4	ND	ND	ND	ND	ND	ND	60
As	19.6	ND	ND	ND	ND	ND	ND	ND
Sm	5.6	9.4	10.8	34.3	5.5	ND	ND	ND
La	33.2	51	61	175	32	ND	ND	ND

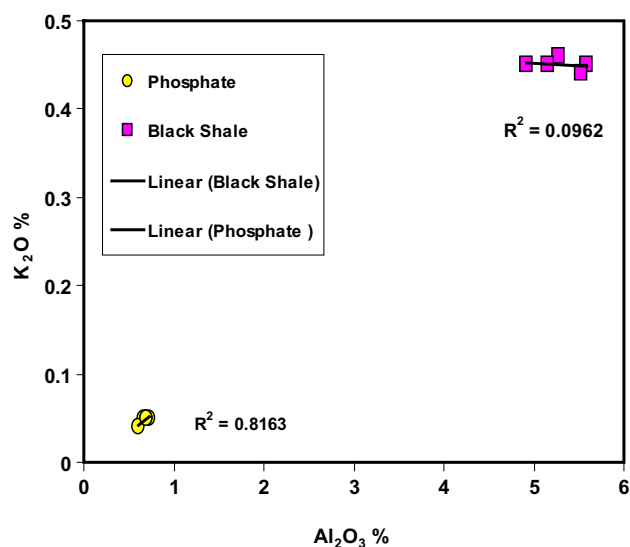
Note: ND = not determined.

between phosphatic rocks and associated rocks in the Duwi Formation, which conforms with Fig. 4. The positive correlation between Cr and Ni ( $r = 0.34$ ) and the Cr/Ni ratios (1.44) revealed that mafic components from the basement source rocks accumulated during weathering.

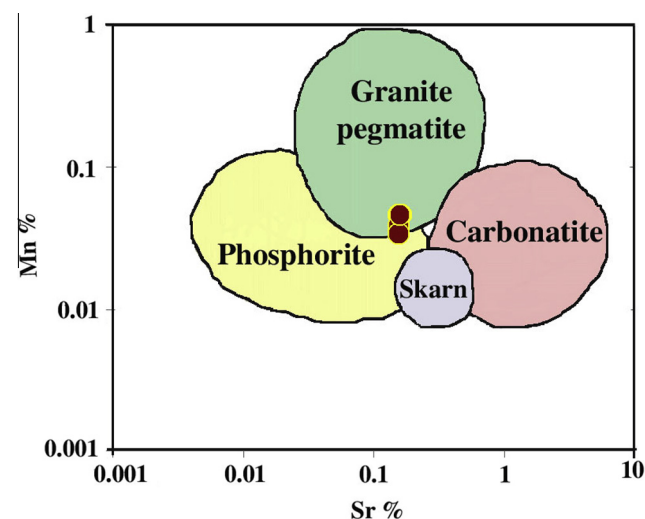
In the Mn versus Sr diagram of Hogarth [48], all the studied phosphatic samples fall on phosphorite overlapping with granite pegmatite fields (Fig. 5). This indicates that the studied phosphates are sedimentary in origin; which conformed with the Sr/P<sub>2</sub>O<sub>5</sub> ratios (Table 1). The lower MgO content in the studied phosphates of the Duwi Formation (average = 0.37%) compared with the Chile and Peru margins authigenic phosphorites (1.5% and 2.3%, respectively) recorded by Baturin and Bezrukov [49], can be attributed to the development of the Duwi phosphates in low MgO sea water. Thus, the environmental conditions of the Duwi phosphatic rocks were formed under those similar to the

phosphatic nodules of Peru and Chile margins. The authigenic phosphorites of the Campanian Mishash Formation in Israel are intercalated with authigenic montmorillonite, which might have reduced Mg ions from the pore-water during early diagenesis [50,7]. Higher SO<sub>3</sub> and F contents compared to the recent authigenic phosphorites indicate that diagenesis plays an important role in the modification of the chemical composition of the studied apatite were francolitized during diagenesis. Generally, during diagenesis the mineralogical composition changes from biogenic apatite to francolite may occur [20]. This change is observed in the Upper Cretaceous of Lanō bones [51]. Consequently, the low Mg and high SO<sub>3</sub> and F contents in the Duwi phosphorites may be attributed to the authigenic phosphorites.

The high enrichments of certain trace elements in sedimentary rocks; Sr, Mo, V, Cr, Zn, Ni and As, are believed to be related to the hydrothermal activity [52,53,16,28]. The enrichment of these trace elements in the studied phosphate rocks indicated that the depositional process may have been coupled with submarine hydrothermal activity derived from mafic



**Figure 4** Al<sub>2</sub>O<sub>3</sub> vs. K<sub>2</sub>O; relation of the studied phosphorites ( $r^2 = 0.8163$ ) and their associated rocks ( $r^2 = 0.0962$ ) (after Abou El-Anwar et al., 2014), [16]. The trend for the phosphorites is different from that for the associated rocks possibly reflecting change in source of detrital influx.



**Figure 5** Mn and Sr content of the phosphate bearing sedimentary rocks compared with apatites in skarn, phosphorites, granite pegmatites and carbonatites from worldwide localities (after Hogarth, 1989), [48].



rocks; which conformed with the recorded values of Mo/Al ratios (Table 1).

## 7. Chemical index of alteration and weathering

According to Nesbitt and Young [54] (CIA) is calculated for the studied phosphorites in order to evaluate the degree of chemical weathering of detrital materials in these rocks, which reflect the climatic condition in the detrital source area. CIA is calculated by the following formula [54]:

$$\text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})] \cdot 100.$$

Table 1 shows low and difference in the values of the Chemical Index of Alteration (CIA) between the studied phosphates (54.61) and the associated black shales (88.16) given by Abou El Anwar et al. [16]. It suggests less intense chemical weathering during the formation of phosphatic rocks, compared with that for the associated black shales in the Duwi Formation (Fig. 6). This could reflect difference in climatic conditions at the time of phosphorite creation either due to the difference in timing or place of formation. This supports that the Duwi phosphatic rocks are derived from pre-existing authigenic phosphorites formed and, then reworked and deposited in the depositional basin later. Fig. 6 shows that the average CIA value (54.61) of the studied phosphates is only comparable with that value for the Red Sea phosphates [7].

## 8. Comparison with other contraries and published averages

Table 4 shows the distribution of the trace and rare earth elements in the studied area and in other different localities in Egypt. The transition metals Fe and Co are more depleted in the studied area than those in Abu Tartur and Nile valley (Fig. 7). However, Co is comparable to this in the Red Sea and Sinai phosphates [55]. The black shales in Quseir area are enriched in all transition metals under control of microbial

activity [45,46,16]). In contrast, Sr, Mo and V as the trace elements and As as rare earth element are highly concentrated in the studied Red Sea samples than in the other localities (Fig. 8).

Table 5 shows that Zn, Co and As concentrations in the studied samples are lower than those in Average World Phosphorite (AWP recorded by Altschuler, [56]). Moreover, the average concentrations for the Ni, Zn, Sr, Cr, Mo and As elements are higher than those in Average Shale Composition (ASC given by Turekian and Wedelpohl, [36]. Ni, Sr, Mo, As and Mn concentrations are much higher compared to those values for the other countries (Table 5 and Fig. 9). But, the Zn and Co values are similar to that determined in phosphate from Jordan [57] and Togo [58].

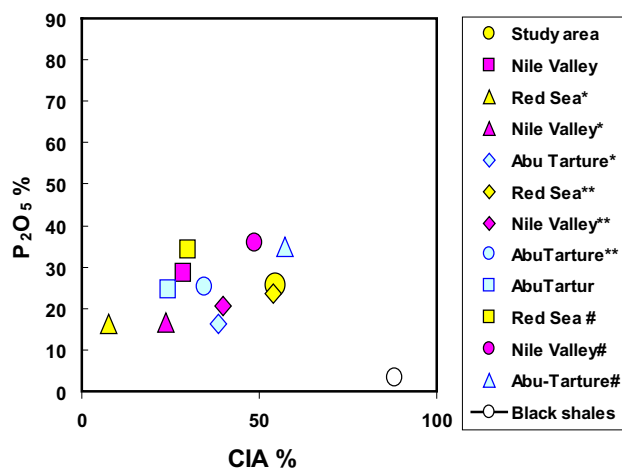
In addition, the phosphates of the Duwi Formation recorded some trace and rare earth elements such as V, La and Sm which are not detected in the other countries, which can be related to the high organic matter content. All the trace elements are below those of the Fertilization Food (Canadian Food Inspection Agency, [59]), expected Mo and As. Compared to the other Middle Eastern–North African phosphorites such as those from Tunisia [21] and Asian phosphorites as those from Jordanian [57], the Upper Cretaceous phosphorites in Egypt, have higher contents of As (19 ppm), (Table 5 and Fig. 9). This value is comparable to the Canadian Food Inspection Agency [59] and lower than those of AWP [56]. Hence, could be the phosphorites in the studied area are suitable for manufacturing fertilizers.

## 9. Utilization of Duwi phosphates

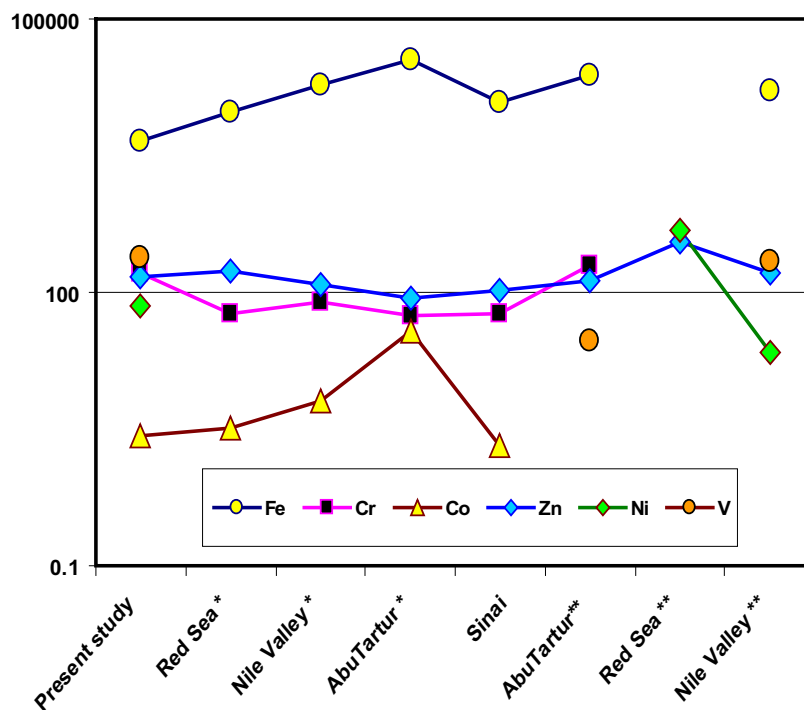
It is necessary in fertilizer industry for the phosphate ores to have (1)  $\text{P}_2\text{O}_5$  content larger than 30%, (2)  $\text{CaO}/\text{P}_2\text{O}_5$  ratio smaller than 1.6, and (3)  $\text{MgO}$  content less than 1% and  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  content; maximum 2.5%.  $\text{P}_2\text{O}_5$  average content of the studied phosphate is  $\sim 26\%$ ,  $\text{MgO}$  content is 0.37% as well as average of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  is 1.34%. The  $\text{CaO}/\text{P}_2\text{O}_5$  ratio of the studied samples shows an average of 2.22. Hence, the studied phosphate samples do not meet all these criteria; it is required to remove their little impurities by some means of beneficiation [6,60].

Some heavy metals are potentially harmful to human health. Accumulation of heavy metals in soil with phosphate fertilizers, cause toxicity to plants, and contaminate the food chain. Cu, Se and Zn are essential to maintain the metabolism of the human body; but they can lead to poisoning at higher concentrations. Heavy metals are associated with a myriad of adverse health effects, including allergic reactions (Be, Cr and Ni), neuro-toxicity (Pb), gastroenteritis, kidney and liver damage (Al), anemia and stomach and intestinal irritation (Cu), and cancer (As) according to Aydin et al. [4]. The use of phosphate rocks may cause environmental hazards because they can contain potentially toxic elements, such as U, Th, REE (rare earth elements), Cd, As, Sb, V, Cr, Zn, Cu, Ni, etc. [21], depending on the presence of these metals, both in crops and in plants.

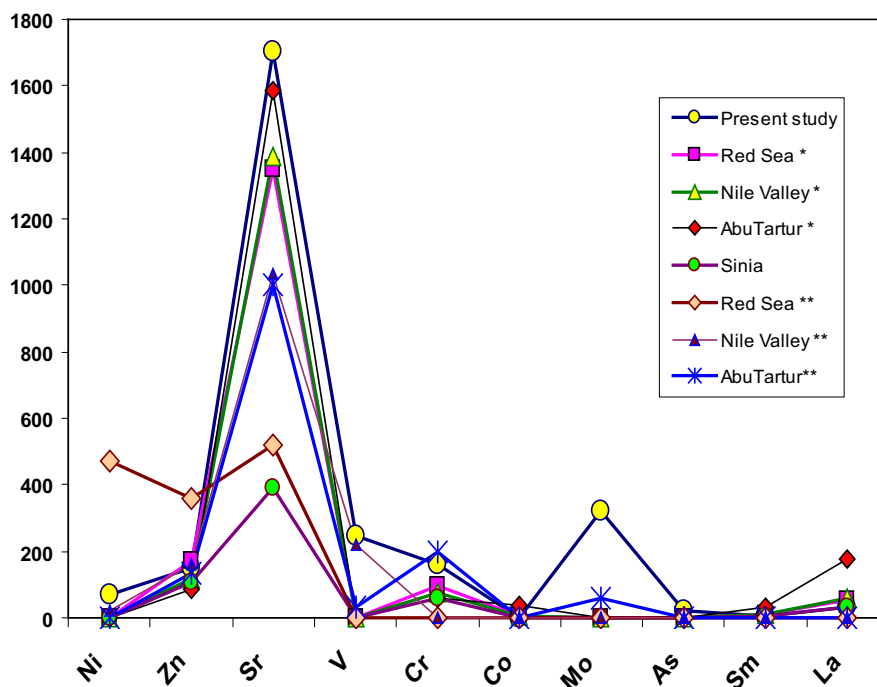
Arsenic and cobalt concentrations in the studied samples are low enough and do not constitute either a health or an environment hazard. According to Dudka and Miller [61] As concentrations can reach 40 ppm without an appreciable toxicological or environmental hazard. Also Co concentrations are



**Figure 6**  $\text{P}_2\text{O}_5$  versus CIA. Nile Valley (Abdel-All and Amer, 1995), [18]; Red Sea\*, Nile Valley\* and Abu Tartur\* (Abd El-Gabar et al., 2002), [9]; Red Sea\*\*, Nile Valley\*\* and Abu Tartur\*\* (Baioumy, 2005) [17]; Red Sea#, Nile Valley# and Abu Tartur# (Baioumy, 2005) [17] and Black Shales Red Sea (Abou El Anwar et al., 2014) [16].



**Figure 7** Average content of the transition metals in the Gebel Duwi Mine compared with other localities in Egypt. Red Sea\*, Nile Valley\* Abu Tartur\* and Sinai (El-Kammar and El-Kammar, 2002) [55] and Abu Tartur\*\*, Red Sea\*\* and Nile Valley\*\* (El-Taher, 2010) [3].



**Figure 8** Trace and rare elemental composition of the phosphates in this study as compared with other localities in Egypt. Red Sea\*, Nile Valley\* Abu Tartur\* and Sinia (El-Kammar and El-Kammar, 2002), [55]; Red Sea\*\* and Nile Valley\*\* (El-Taher, 2010), [18] and Abu Tartur\*\* (Awad Alla, 2011), [15].

sufficiently low to cause any health or environmental risk. According to Sabila-Javied et al. [62] the toxic effects on plants are unlikely to occur if Co concentrations are below 40 ppm,

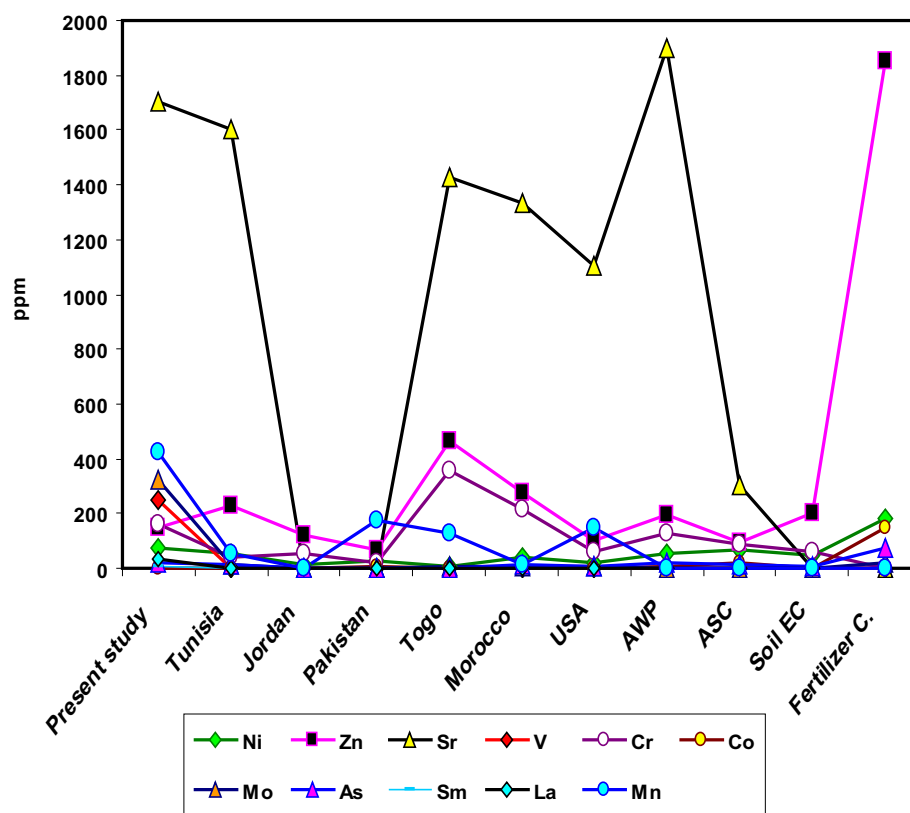
but small amounts are required for plant growth (3 ppm). Ni concentrations are below the tolerable limit of compatible and safe with respect to Ni [62]. The average value for Zn,

**Table 5** Trace and rare earth elemental composition of the phosphates in this study as compared with other published average phosphates.

Element ppm	Present study	Tunisia	Jordan	Pakistan	Togo	Morocco	USA	AWP	ASC	Soil EC	Fertilizer C.
Ni	72	55	15	28	8.5	41.4	17.7	53	68	50	180
Zn	149	226	121	67.2	465	279	104	195	95	200	1850
Sr	1705	1606	n.a.	n.a.	1429	1331	1104	1900	300	n.a.	n.a.
V	246	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Cr	161.4	42.7	51	17	356	217	62.6	125	90	60	n.a.
Co	2.6	0.3	n.a.	9.4	2.5	0.75	2.83	7	19	n.a.	150
Mo	323.4	14.1	n.a.	n.a.	8.5	7.9	6.68	n.a.	2.5	n.a.	20
As	19.6	11	n.a.	n.a.	n.a.	10.7	7.7	23	13	8	75
Sm	5.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
La	33.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Mn	422	51.2	n.a.	178	126	15	148	n.a.	850	n.a.	n.a.
U	35	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Note: n.a. = not available.

AWP, Average World Phosphorite by Altschuler [56]; ASC, Average Shale Composition by Turekian and Wedelpohl [36]; Soil EC, Permissible limit established by the Soil EC Directive (European Commission EC, 1986), [43]; Fertilizer Canada, Permissible limit established by the Canadian Food Inspection Agency [59]; Tunisia (de Silva et al., 2010), [21]; Jordan (Batarseh and El-Hasan, 2009), [57]; Togo (Gnandi et al., 2006), [58]; Morocco (Suttouf 2007), [19]; Pakistan (Sabiha-Javied et al., 2009), [62] and USA (Suttouf 2007), [19].



**Figure 9** Trace and rare elemental composition of the phosphates in this study as compared with other published average phosphates. AWP, Average World Phosphorite by Altschuler (1980), [56]; ASC, Average Shale Composition by Turekian and Wedelpohl (1961), [36]; Soil EC, Permissible limit established by the Soil EC Directive (European Commission EC, 1986), [43]; Fertilizer Canada: Permissible limit established by the Canadian Food Inspection Agency (1997), [59]; Tunisia (de Silva et al., 2010), [21]; Jordan (Batarseh and El-Hasan, 2009), [57]; Togo (Gnandi et al., 2006), [58]; Morocco (Suttouf 2007), [19]; Pakistan (Sabiha-Javied et al., 2009) [62] and USA (Suttouf, 2007) [19].

Co and As concentration in the studied samples are considered to be very positive for most field-grown crops.

This study should lead to a better understanding of the distribution of the potentially toxic elements in the Duwi

Formation; finally, evaluate their impact to the environment and human health. Consequently, it is required to remove their impurities by some means of beneficiation for using as ores.

## 10. Conclusion

In Egypt, phosphate bearing strata of economic importance and associated shales of the Duwi Formation are stretching from the Red Sea Coast in Quseir over the Nile Valley into the Western Desert in Abu Tartur. The deposition of the phosphatic beds associated with black shales clearly demonstrates a transgression from the east to the west, starting in the Eastern Desert during the Lower Campanian and end in the Upper Campanian and Lower Maastrichtian. The Duwi Mine phosphorites are considered as the highest grade (attain average of ~26% P<sub>2</sub>O<sub>5</sub>). The studied phosphate samples show enrichment in P<sub>2</sub>O<sub>5</sub>, CaO and F, which reveals that fluorapatite is the main phosphate mineral in the studied area. The low content of the detrital terrigenous influx Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, and the association of the phosphate beds with oyster limestone and diatom enrichment in Quseir indicates to the marine origin of the phosphates in the Eastern part of Egypt. Fe<sub>2</sub>O<sub>3</sub> contents of the studied phosphate indicate the formation of phosphate in the near-surface oxidizing environment. The distribution of many trace elements has been affected by weathering. The studied phosphates show higher contents of the trace elements Sr, Co, As and La than in the associated black shales. The Duwi Mine phosphorites show the highest enrichment of Mo, V, Cr, Zn and Ni due to the oxidation and weathering of the organic matter and subsequent mobilization and concentration of these trace elements. The enrichment in the studied phosphate samples indicates leaching processes outgoing from the overlying and/or underlying black shales. The intensive post-depositional diagenetic processes, led to liberation of uranium from the apatite lattices and migration to the phosphorite beds. The abundance of the transition metals in phosphorites seems to be controlled by the terrigenous influx to the depositional basins. The concentrations of the elements determined in the present study lie within the worldwide range of these elements. However, like other phosphorites elsewhere in the world, they are highly enriched in several heavy elements, such as Mn, Cr, Mo, Ni, and Zn, and REEs. From these results it was concluded that rock phosphate can be used as a crude phosphate fertilizer.

## References

- [1] M.B. Tariq, W. Yawar, *Hydrometallurgy* 103 (2010) 54–59.
- [2] A.Z.M. Abouzeid, *Int. J. Miner. Process.* 85 (2008) 59–84.
- [3] A. El-Taher, *Appl. Radiat. Isot.* 68 (2010) 511–515.
- [4] I. Aydin, F. Aydin, A. Saydut, G. Bakirdere, C. Hamamci, *J. Microchem.* 96 (2010) 247–251.
- [5] A.K. Ozer, M. Gulaboglu, S. Bayrakceken, *Ind. Eng. Chem. Res.* 39 (2000) 679–683.
- [6] H. Sengul, A.K. Ozer, M.S. Gulaboglu, *Chem. Eng. J.* 122 (2006) 135–140.
- [7] H. Baioumy, R. Tada, *Cretaceous Res.* 26 (2005) 261–275.
- [8] A.A. Tantawy, G. Keller, T. Adatte, W. Stinnesbeck, A. Kassab, P. Schulte, *Cretaceous Res.* 22 (6) (2001) 795–827.
- [9] M. Abd El-Gabar, I. El-Arabia, H. Khalifa, *Egypt. J. Environ. Radioact.* 6 (2002) 169–190.
- [10] M. Abdel-Rahman, *Geochemical, mineralogical and sedimentological studies on phosphorites of the Nile Valley (Duwi Formation) between Qena and Idfu, Egypt (Ph.D. thesis), Technischen University, Berlin, Germany, 1992, p. 163.*
- [11] M.G. Temraz, *Mineralogical and geochemical studies of carbonaceous shale deposits from Egypt (Ph.D. thesis), Berlin Unvi., 2005, p. 124.*
- [12] H. Ganz, U. Troger, F. Oner, *Berl. Geowiss. Abh. A* 75 (3) (1987) 691–698.
- [13] M. Faris, *Micropdeontologie et biostratigraphie du Cretace Superier l'Eocene Inferiew de l' Egypt centale region de Duwi valle du Nil, Oasis de Kharga et de Dakhla (These d'Etat.), Univ. Paris, Paris, 1982, p. 438.*
- [14] G.F. Malash, M.I. El-Khaiary, *J. Colloid Interface Sci.* 348 (2010) 537–545.
- [15] G.S. Awadalla, *J. Afr. Earth Sci.* 57 (2011) 431–443.
- [16] E.A. Abou El-Anwar, H.S. Mekky, Y.M. Samy, *Egypt. J. Geol.* 58 (2014) 303–322.
- [17] H.M. Baioumy, *J. Afr. Earth Sci.* 41 (2005) 266–274.
- [18] E.A. Abdel-All, A.M. Amer, *Miner. Eng.* 8 (10) (1995) 1221–1230.
- [19] M. Suttouf, *Identifying the Origin of Rock Phosphates and Phosphorus Fertilisers Using Isotope Ratio Techniques and Heavy Metal Patterns*[nl]Von der Fakultat fur Lebenswissenschaften der Technischen Universitat Carolo-Wilhelmina, Doktors der Naturwissenschaften, 2007, 196.
- [20] J.F. Hubert, P.T. Panish, D.J. Chure, K.S. Probst, *J. Sediment. Res.* 66 (1996) 531–547.
- [21] E.F.D. de Silva, M. Ammar, G. Celso, N. Fernando, C. Abdelkrim, S. Cristina, E. Valdemar, R. Ana, F. Marques, *J. Hazard. Mater.* 182 (2010) 232–245.
- [22] G. Einsale, *Sedimentary basins: Evolution, Facies, and Sediment Budget*, Springer, Berlin, Heidelberg, 1992, p. 628.
- [23] K. Germann, W.D. Bock, H. Ganz, T. Schröter, U. Tröger, *Depositional conditions of Late Cretaceous phosphorites and black-shales in Egypt, Berl. Geowiss. Abh. A* 75 (3) (1987) 629–668.
- [24] P.W. Choquette, N.P. James, *Limestone-the burial diagenetic environment*, in: *Diagenesis*, in: I.A. McIlreath, D.W. Morrow (Eds.), *Geoscience Canada Reprint Series*, 4, 1990.
- [25] W.E. Krumbein, *Microbial geochemistry*, Blackwell Scientific Publ., 1983, p. 330.
- [26] E.A. Abou El-Anwar, *Sedimentol. Egypt* 13 (2005) 243–260.
- [27] E.A. Abou El-Anwar, *Bull. NRC Egypt* 32 (5) (2007) 511–536.
- [28] E.A. Abou El-Anwar, *Carbonates Evaporites* (2014), <http://dx.doi.org/10.1007/s13146-014-0188-3>.
- [29] E.A. Abou El-Anwar, H.S. Mekky, *J. Appl. Sci. Res.* 9 (6) (2013) 3659–3673.
- [30] J. Pan, H. Xiaoxiao, N. Wenjuan, R.E. Cameron, *Biomaterials* 32 (2011) 2248–2255.
- [31] P.C. Delaney, Mc J.P. Hanrahanb, M.P. Copleya, J.D. Holmesa, M.A. Morris, *J. Hazard. Mater.* 185 (2011) 382–391.
- [32] H. Singh, M. Sudhakara Reddy, *Eur. J. Soil Biol.* 47 (2011) 30–34.
- [33] M. Nieminen, A. Laurén, H. Hökkä, S. Sarkkola, H. Koivusalo, T. Pennanen, *For. Ecol. Manage.* 261 (2011) 105–110.
- [34] O. Cuisinier, T. Borgne, D. Deneele, F. Masrour, *Eng. Geol.* 117 (2011) 229–235.
- [35] A.M. El-Kammar, M.A. Zayed, S.A. Amer, *Chem. Geol.* 24 (1979) 69–81.
- [36] K.K. Turekian, K.H. Wedelpohl, *Geol. Soc. Am. Bull.* 72 (1961) 175–192.
- [37] N.T. El Hazek, E.R. Philobos, W.W. Bishara, M.F. Mohamed, *Bull. Fac. Sci. Assiut Univ.* 9 (1) (1980) 159–189.
- [38] E.A. Abou El-Anwar, *Int. Conf. on Geological Sciences and Engineering, Farance, Paris* 80 (2011) 1315–1325. Augustus 24–26.
- [39] T.J. Algeo, J.B. Maynard, *Chem. Geol.* 206 (2004) 289–318.
- [40] S.R. Taylor, S.M. McLennan, *The Continental Crust: Its Composition and Evolution*, Blackwell, Oxford, 1985, p. 312.
- [41] P. Dao-Hui, L. Cong-Qiang, G. Shields-Zhoud, J. Shao-Yong, *Precambrian Res.* 225 (2013) 218–229.
- [42] K.F. Khan, A. Shamim, A. Dar Khan, *Chem. Erde* 72 (2012) 117–125.

- [43] European Commission (EC), Council Directive (86/278/EEC) on the protection of the environment, and in particular of soil, when sewage sludge is used in agriculture, Official J. European Community L181 (Annex 1A), 1986, pp. 6–12.
- [44] P.N. Froelich, M. Arthur, W.C. Burnett, M. Deakin, V. Hensley, R. Jahnke, L. Kaul, K. Kim, K. Roe, A. Soutar, C. Vathkanon, Early diagenesis of organic matter in Peru continental margin sediments: phosphorite precipitation, in: *Origin of Marine Phosphorite. The results of R.V. Robert D*, in: W.C. Burnett, P.N. Froelich (Eds.), *Conrad cruise 23-06 to the Peru shelf. Mar. Geol.*, 80, 1988, pp. 309–343.
- [45] A.M. El-Kammar, M. Darwish, G. Phillip, M.M. El-Kammar, *J. Univ. Kuwait Sci.* 17 (1990) 177–190.
- [46] M.S. Abou El-Anwar, M.S. El-Sayed, *Bull. NRC Egypt* 32 (5) (2008) 511.
- [47] S.k. Aita, S.A. Abu Elatta, M.E. Darwish, *Sedimentol. Egypt* 21 (2013) 119–130.
- [48] D.D. Hogarth, Pyrochlore, apatite and amphibole: distinctive minerals in carbonatite, in: K. Bell (Ed.), *Carbonatites: genesis and evolution*, Unwin Hyman, London, 1989, pp. 105–148.
- [49] G.N. Baturin, P.L. Bezrukov, *Marine Geol.* 31 (1979) 317–332.
- [50] D. Soudry, *Sediment. Geol.* 80 (1992) 77–88.
- [51] J. Elorza, A. Humberto, M. Xabier, X. Pereda-Suberbiola, *Cretaceous Res.* 20 (1999) 169–187.
- [52] T. Angerera, R. Kerrichb, G. Steffen, *Precambrian Res.* 224 (2013) 110–128.
- [53] E. Vindel, C. Eva, V. Carlos, L.-G. Ángel, V. Sánchez, *Ore Geol. Rev.* 62 (2014) 143–155.
- [54] H.W. Nesbitt, G.M. Young, *Nature* 299 (1982) 715–717.
- [55] A.M. El-Kammar, M.M. El-Kammar, in: *Proceeding of the 6th International Conference of the Arab World*, Cairo University, 2002, pp. 227–244.
- [56] Z.S. Altschuler, The geochemistry of trace elements in marine phosphorites. Part I. Characteristic abundances and enrichment, in: Y.K. Bendor (Ed.), *Marine Phosphorites*, SEPM Spec Publ, 1980.
- [57] M. Batarseh, T. El-Hasan, *An Int. J.* 18 (2) (2009) 205–215.
- [58] K. Gnandi, G. Tchchangbedji, K. Killi, G. Baba, K. Abbe, *Mine Water Environ.* 25 (2006) 56–62.
- [59] Canadian Food Inspection Agency, Plant Production: fertilizers section, Website: [www.inspection.gc.ca/English/plaveg/fereng/tememo/t-4-83.shtml](http://www.inspection.gc.ca/English/plaveg/fereng/tememo/t-4-83.shtml), 1997.
- [60] T. Heidarpour, Processing of Dalir phosphate samples using leaching method (M.Sc thesis), Department of Mining & Metallurgical Engineering, Amirkabir University of Technology, Iran, 2009.
- [61] S. Dudka, W.P. Miller, *Water Air Soil Pollut.* 113 (1999) 127–132.
- [62] T. Sabiha-Javied, M.M. Mehmood, M. Chaudhry, S. Tufail, N. Irfan, *Microchem. J.* 91 (2009) 94–99.