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## DETERMINATION OF PHOSPHATE ROCK MINES SIGNATURES USING XRF AND ICP-MS ELEMENTAL ANALYSIS TECHNIQUES: RADIONUCLIDES, OXIDES, RARE EARTH, AND TRACE ELEMENTS

ATEF EL-TAHER<sup>1,2</sup>, AHMED ASHRY<sup>3</sup>, ANTOANETA ENE<sup>4,\*</sup>,  
MESHARI ALMESHARI<sup>5</sup>, HESHAM M.H. ZAKALY<sup>1,6,\*</sup>

<sup>1</sup> Physics Department, Faculty of Science, Al-Azhar University, Assuit Branch, 71524 Assuit, Egypt

<sup>2</sup> Department of General Educational Development, Faculty of Science and Information Technology, Daffodil International University Ashulia, Dhaka 1341, Bangladesh

<sup>3</sup> Radiation Protection Department, Nuclear Research Center, Egyptian Atomic Energy Authority, P.O. Box 13759, Cairo, Egypt

<sup>4</sup> Dunarea de Jos University of Galati, INPOLDE research center, Department of Chemistry, Physics, and Environment, 47 Domneasca Street, 800008 Galati, Romania  
E-mail: [Antoaneta.Ene@ugal.ro](mailto:Antoaneta.Ene@ugal.ro)

<sup>5</sup> Department of Diagnostic Radiology, College of Applied Medical Sciences, University of Ha'il, Ha'il, Saudi Arabia

<sup>6</sup> Institute of Physics and Technology, Ural Federal University, Ekaterinburg 620002, Russia

\* Corresponding authors: [Antoaneta.Ene@ugal.ro](mailto:Antoaneta.Ene@ugal.ro); [h.m.zakaly@azhar.edu.eg](mailto:h.m.zakaly@azhar.edu.eg)

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**Abstract.** Inductively coupled plasma mass spectrometry (ICP-MS) was used to provide precise information on the fundamental elemental compositions of phosphate rocks from the El-Sibayia and El-Hamrawein mines in Egypt. To create an elemental fingerprint for the two locations under examination, twenty-five elements were determined (U, Th, Eu, Hf, La, Lu, Sm, Tb, Yb, Ce, Dy, Er, Nd, Pr, Tm, Zn, Cu, Pb, Ni, Co, Cd, Sc, Ag, Li, and Mo). The concentrations of radioelements (uranium, thorium), rare earth elements (REEs), and other trace elements and heavy metals in the phosphate samples under inquiry were compared to those found in other published work. The X-ray fluorescence method (XRF) was used to identify the various oxides found in phosphate rocks: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, Cr<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, MnO, SrO and BaO. The data will be used to create a baseline level for these elements in phosphate rocks, as well as to assess the agronomic viability of the phosphate extracted from the El-Sibayia and El-Hamrawein mines.

**Key words:** REE, radionuclides, metals, phosphate mines, Egypt, ICP-MS, EDXRF.

### 1. INTRODUCTION

Natural phosphates are well-known for being constituted of a variety of stable and radioactive elements that have the potential to be hazardous to the general people and their health when seen from an environmental perspective [1–4]. The potential pollutant elements (heavy metals, radioisotopes, microelements) existing in the phosphate material can migrate from soil to groundwater and crops [5–8] or

to surface waters affecting the specific biota [4]. Phosphate minerals are mostly constituted of calcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$  and are thought to be ancient marine storage that are associated to fossilized organisms. Approximately 85 percent of the world's reservoirs are comprised of this sort of mineral. Phosphate apatite (red hot rocks) is the second most abundant phosphate rock on the planet, behind phosphate feldspar [9, 10]. There are two types of phosphate rocks: sedimentary rocks – found primarily in North Africa and the Middle East (Morocco, Saudi Arabia, and Tunisia) – and metamorphic rocks (which include phosphate rocks) [11, 12]. In contrast, Russia and South Africa are profoundly abundant in igneous rocks.

Sedimentary rocks exhibit high convergence of substantial metals – U, Th, rare earth elements (REEs) – alongside polluting ecological components: Cd, As, Sb, Zn, Cu, Ni, Cr and V [11, 13]. Uranium could move from phosphate minerals and composts to soil-plant interfaces and, in this manner, to people *via* the natural food chain in different forms including water, plant, and animal, in which the presence of radionuclides and toxic heavy metals may bring about antagonistic impacts [14, 15].

Phosphate rock elemental compositions are largely dependent on their source. Sedimentary rocks, for example, are generally high in toxic elements [11]. Phosphate-bearing rock does not contain only many essential terrestrial and industrial components, such as REEs, but it stores many toxic elements, such as Cd, Hg, As, Th, Sb and Pb, etc. [6, 11, 16]. One of the characteristics of phosphate origins is the content of REEs and other rare elements in phosphates and their ratios can define the source of phosphate rocks. Such data could be used in the field of applied geochemistry for the characterization of apatite-bearing rocks and ores and applying effective methods for evaluating the presence of hazardous elements in rocks but, in the same time, of technologically valuable elements such as lanthanides [8, 10, 12, 17].

In order to characterize an element's environmental status, appropriate compositional scheme analysis should be established in geology, mineralogy and environmental risk assessment studies, based on accurate and sensitive atomic, nuclear and nuclear-like techniques, such as: X-ray fluorescence (XRF) (including energy-dispersive XRF (EDXRF)), instrumental neutron activation analysis (INAA), inductively coupled plasma mass spectrometry (ICP-MS), particle-induced X-ray emission (PIXE) and atomic absorption spectrometry (AAS) [11, 18–28].

Information about the phosphates extracted from the mines from the Nile Valley – Red Sea axis in Egypt is very scarce, several papers focusing on the radioactivity of the phosphate rocks [29–31] and their trace and major elemental composition [12, 14, 17, 23]. The purpose of this work was to evaluate the elemental (radioelements, REEs, metals, oxides) composition and distribution in phosphate rocks from El-Sibaiya and El-Hamrawein mines, Egypt, by using combined ICP-MS and EDXRF techniques. Our work will contribute to the completion of the database related to multi-elemental fingerprint of Egyptian phosphate rocks, useful in the sustainable exploration and exploitation of these raw material resources of crucial importance, both from the economic and mining waste management point of view.

## 2. GEOLOGICAL SETTING

During the Late Cretaceous, the Campanian-Maastrichtian Duwi Formation in Egypt represents a section of the Middle Eastern and North African phosphate province that existed at the time. This location is home to the largest concentration of phosphates in topographical history, perhaps exceeding 70 billion metric tons of the mineral. Egypt's phosphate holdings include more than 3 billion metric tons of reserves. Duwi Formation is characterized primarily by phosphate sedimentation, which is highly associated with the Upper Cretaceous-Lower Cenozoic sedimentary succession [8, 10, 12, 15, 29, 32]. It has been widely appropriated in many areas of Egypt, including the Eastern Desert, the Nile Valley, and the Western Desert, among other places. In the lower-center of Campanian Quseir Formation, the Duwi Formation overlies the fluvial shale succession of the Quseir Formation (variegated shales), and it underlies the lower Maastrichtian-Upper Paleocene Dakhla Formation. The Duwi Formation, as a result, was primarily responsible for the development of the Late Cretaceous maritime environment in Egypt. It has been discovered that the lithofacies of the Duwi Formation, located between the Red Sea, Nile Valley, and Western Desert zones, exhibit territorial and local variation. Specifically, two mines (El-Sibaiya and El-Hamrawein) were selected for this inquiry, as seen in Fig. 1. The first is located in the Nile Valley (the El-Gidida section), while the second is located on the Red Sea coast (El-Hamrawein section). The Duwi Formation overlies the Quseir Formation in both portions, and the two formations have properties that are comparable between them.



Fig. 1 – Map of the investigated phosphate mines in Egypt.

Located in the Nile Valley, the Duwi Formation starts with a thick bed of pebbly phosphate that ranges in color from yellow to yellowish dull, with an average thickness of 3 meters (Fig. 2a) [10, 29, 32]. This is followed by limestone clams that are black in coloring with a thin layer of phosphate 10 cm thick between them. The lime content was discovered to be medium-hued steel, light yellow in color, with a thickness of around 1.5 m, covered by a thin layer of approximately 10 cm in thickness at the top. The phosphate content has been restored, and the rock is characterized by a dim to earthy dark color, medium hardness, and iron oxides covering its surface; its thickness is 20 cm. The Duwi Formation, which overlies the variegated shale of Quseir and lies under the Shale of Dakhla, may be also found on the Red Sea coast, at the El-Hamrawein mine. It is composed of shale interbedded with marls clay and carbonates, which include various phosphate minerals, as well as shale (Fig. 2b) [10, 29, 32].

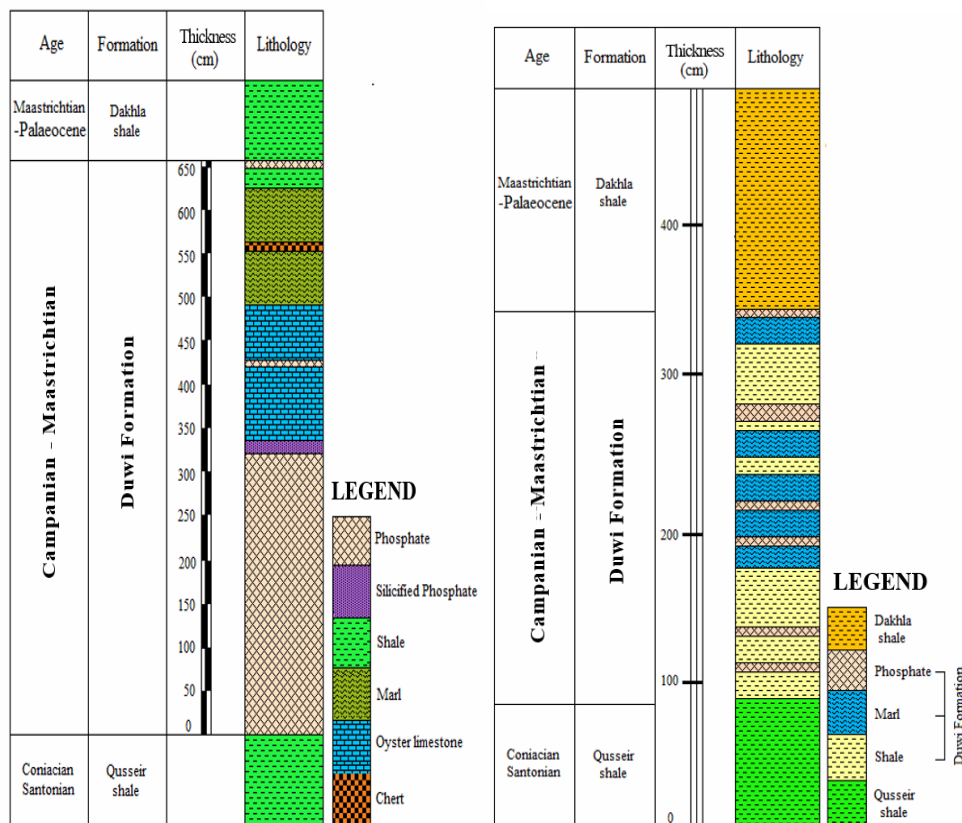


Fig. 2 – Columnar section of Duwi formation exposed in: a) Nile valley (El-Gidida section); b) Red Sea coast (El-Hamrawein section). Compilation after [10, 29, 32].

### 3. SAMPLES PREPARATION AND ANALYSIS

Thirteen samples of phosphate ores were gathered from the El-Sibayia and El-Hamrawein mines in Egypt, with the majority coming from the latter spot. Finely ground and homogeneous material was produced from these samples and subjected to analysis.

ICP-MS studies were performed using an aliquot of the material (0.1 g), which was mixed well and fused at 1025 degrees Celsius in a furnace prior to being analyzed. The melt that formed as a consequence of fusion was allowed to cool to room temperature before being dissolved in a combination of various acids (*i.e.*, nitric, hydrochloric, and hydrofluoric acids). The elements in this resultant solution were subsequently studied and quantified using the Perkin-Elmer Elan 9000 ICP-MS equipment at the ALS-Chemex Laboratory in Vancouver, Canada, which is owned by Perkin-Elmer. The laboratory was accredited as an ISO 9001:2000 lab for "provision of assay and geochemical analytical services" [17]. The application of quality control methods was carried out with the use of reference materials, blanks, duplicate analyses, and proficiency tests that were obtained from a third party and held outside. Precision is stated to be within  $\pm 10\%$  of the applied geochemical processes, with assay methods having a precision of within  $\pm 5\%$  of the applicable geochemical procedures.

For the oxides analysis, an EDXRF spectrometer from ARL Quant'X, Thermo Scientific Inc. manufacturer, USA, was utilized, having an X-ray tube anode material made up of rhodium. High-energy X-rays collided with the substance under investigation (phosphate rocks samples), causing the excitation of atoms in the material samples subjected to analysis. The applied voltage was in a range from 4 to 50 kV. The detector material was made from the Si (Li) semiconductor, having a cylindrical shape with a 15 mm<sup>2</sup> cylindrical region and a 3.5 mm cylindrical depth.

## 4. RESULTS AND DISCUSSION

### 4.1. DETERMINATION OF OXIDES CONCENTRATIONS

Table 1 shows the percentages of oxides compositions in phosphate rocks from Egypt's El-Sibayia and El-Hamrawein phosphate formations. The concentrations of the identified oxides ranged from 0.01 to 45.8 percent for El-Sibayia and from 0.02 to 42.8 percent for El-Hamrawein, respectively. Calcium oxide was found to have the greatest mean content in the El-Sibayia and El-Hamrawein samples, which is not surprising since it is the primary component of several minerals, including calcite and dolomite, francolite, and gypsum. The total concentration of calcite was calculated using the total calcium oxide, adjusted by a fraction to the contribution of calcium oxide by dolomite. As a result, the uncertainty in calcite

samples calculation is dependent on the uncertainty in the measurements of calcium oxide concentration, as well as from  $\text{Al}_2\text{O}_3$  (which is used to calculate the detrital fraction concentration),  $\text{P}_2\text{O}_5$  (as a measure of apatite concentrations), and MgO (as a measure of the detrital fraction concentration). The mean concentrations of oxides in the samples from El-Sibaiya –  $\text{K}_2\text{O}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$ , MnO, SrO, and BaO – were found to be very low, with mean concentrations ranging from 0.01 to 0.23 percent, whereas the mean concentrations in the samples from El-Hamrawein varied from 0.02 to 0.20 percent.

Table 1

Comparison between the fixation estimations of oxides from El-Sibaiya and El-Hamrawein (Egypt) with phosphate shake from different spots

Oxides composition (%)	El-Sibaiya (This study)	El-Hamrawein (This study)	Egypt (Gebel Qulu El Sabaya) [12]	Saudi Arabia (Umm Waal) [14]	Saudi Arabia (El-Jalamid) [14]
$\text{SiO}_2$	6.69	14.95	7.19	2.1	2.79
$\text{Al}_2\text{O}_3$	0.48	0.64	1.84	0.15	0.33
$\text{Fe}_2\text{O}_3$	2.09	1.44	4.18	0.19	0.26
CaO	45.8	42.8	38.35	52.8	50.4
MgO	0.22	0.25	3.99	0.16	2.35
$\text{Na}_2\text{O}$	0.64	0.54	1.33	0.84	0.27
$\text{K}_2\text{O}$	0.06	0.07	0.22	0.03	0.04
$\text{Cr}_2\text{O}_3$	0.01	0.02	–	0.02	0.01
$\text{TiO}_2$	0.04	0.04	–	0.01	0.02
MnO	0.06	0.04	–	0.01	0.01
$\text{P}_2\text{O}_5$	27.6	24.3	24.92	33.1	21.25
SrO	0.23	0.2	–	0.13	0.05
BaO	0.06	0.07	–	0.01	0.01

Table 1 also includes a comparison of the concentration values of oxides from El-Sibaiya and El-Hamrawein phosphate rocks with other locations in Egypt [12] and Saudi Arabia [14]. Generally, the concentration of oxides from El-Sibaiya and El-Hamrawein, Egypt, were found to be greater than the values of El-Jalamid and Umm Waal in Saudi Arabia [14], with the exception of CaO, MgO and  $\text{Na}_2\text{O}$ . The amounts of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , MgO,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  from this work are lower than those reported for Gebel Qulu mine [12], while the  $\text{P}_2\text{O}_5$  concentration is comparable, denoting a medium grade ore deposit in El-Hamrawein (23–27% of  $\text{P}_2\text{O}_5$ ) and a high grade deposit in El-Sibaiya (> 27%  $\text{P}_2\text{O}_5$ ) [12].

#### 4.2. DETERMINATION OF URANIUM, THORIUM, AND RARE EARTH ELEMENTS

Phosphate rocks are distinguished by the presence of radioactive elements in large quantities, and they are classified as uraniferous phosphorites. The radioactive properties of these rocks are mostly due to the close proximity of phosphatic segments,

which facilitate the entry of uranium into the rock, as well as the presence of apatite minerals in the rock. Apatite grid liberation was caused by severe post-depositional diagenetic processes, which led to uranium relocation from the cross-sections of apatite grids and its repositioning within the host rocks. This was the first step in uranium release from apatite grids [17]. Due to a replacement somewhere in the range of Ca(II) and U(IV) in the apatite cross-section, the U has been locked in position [33, 34].

Table 2 lists the U, Th, and REEs (Eu, Hf, La, Lu, Sm, Tb, Yb, Ce, Dy, Er, Nd, Pr and Tm) concentrations found in phosphate tests conducted in the El-Sibaiya and El-Hamrawein, expressed in parts per million (ppm), determined by ICP-MS. U concentrations in tests from El-Sibaiya mines are greater than in El-Hamrawein mines, while the concentrations of Th are comparable in the two sites. The average U concentrations in the examined locations was in the lower section of the entire range of U fixation in phosphate (50–300 mg/kg) from various countries throughout the world, fact which is consistent with previous findings [4, 11, 17, 29, 30, 35, 36].

Table 2

Average concentrations of radioelements (uranium, thorium) and REEs in phosphate rocks from El-Sibaiya and El-Hamrawein (Egypt)

Element	Concentration (ppm)	
	El-Sibaiya	El-Hamrawein
U	87.7	81.5
Th	1.68	1.71
Eu	2.15	1.59
Hf	0.33	0.4
La	45.85	34.1
Lu	0.81	0.57
Sm	8.06	6.02
Tb	1.3	1.02
Yb	5.5	3.77
Ce	62.53	48.9
Dy	8.21	6.12
Er	5.82	4.18
Nd	34.33	27.7
Pr	8.78	6.84
Tm	0.86	0.63
$\Sigma$ REE	184.53	141.84
Eu/Sm	0.27	0.26
Ce/La	1.36	1.43



REEs from El-Sibaiya ranged from 0.33 to 62.53, while in samples from El-Hamrawein mines ranged from 0.40 to 48.9 ppm. The lowest REE concentrations were recorded for Hf in all samples. The (Eu/Sm) and (Ce/La) ratio is a measure of the degree of fractionation of the Light (LREE) relative to the Heavy (HREE) REEs. From the results in Table 2, the  $\sum$ REE values varied from 124.87 ppm in samples from El-Sibaiya mine to 96.37 ppm in samples from El-Hamrawein mines. Since REEs have been utilized as a mark on the source of pollution and have been seen to be stored in phosphates, the distinguishing proof of REEs in phosphate rocks can be a valuable commitment to understanding the enduring and tests of these stones [24]. The variety in the REEs fixation in these stones may be due of topographical procedures associated with shake arrangement bringing about the consumption or improvement of the REE components [11]. By contrast, this fixation and the normal composition of REEs found in shooting stars (chondrites) [La:0.300, Ce:0.840, Sm:0.210, Eu:0.074, Tb:0.049, Yb:0.170, Lu:0.031 ppm], North American Shales [La:39.00, Ce:76.00, Sm:7.00, Eu:2.00, Tb:1.30, Yb:3.40, Lu:0.60 ppm], Western American Precambrian granites [La:49.00, Ce:97.00, Sm:7.20, Eu:1.25, Tb:0.94, Yb:3.50, Lu:0.52 ppm] and Kilauea basalt [La:10.50, Ce:35.00, Sm:4.20, Eu:1.31, Tb:0.66, Yb:1.11, Lu:0.20 ppm], indicated that in chondritic (granular) meteorites the relative values of the rare earth elements represent their overall relative abundance in the cosmos. Several research studies have shown that many REEs are declining in the acidic, Fe-rich crustal region, despite the fact that they are incredibly adaptable and progressed in more deep zones [37].

#### 4.3. DETERMINATION OF TRACE ELEMENTS AND HEAVY METALS

Ten metals (Zn, Cu, Pb, Ni, Co, Cd, Sc, Ag, Li, and Mo) were quantified in phosphate rocks from the El-Sibaiya and El-Hamrawein mines and their concentrations are shown in Table 3.

Table 3

Average concentrations (ppm) of trace elements in phosphate rocks (El-Sibaiya and El-Hamrawein)

Element	El-Sibaiya	El-Hamrawein
Cd	10.5	9.8
Co	<1	<1
Cu	12	9
Ni	23	17
Pb	5.6	4
Sc	8	5
Zn	264	235
Ag	<0.5	<0.5
Li	<10	<10
Mo	8	7

Samples from El-Sibaiya mine included higher amounts of cadmium, copper, lead, nickel, zinc, aluminum, lithium, and molybdenum, than the samples from El-Hamrawein mine.

In terms of environmental pollution, compared to the composition reported in other regions [4, 11, 12, 17, 23], the phosphate rocks from the El-Sibaiya and El-Hamrawein mines have a lower concentration of the components and are becoming increasingly feasible for use in farming as an alternative to phosphate fertilizers produced on the basis of phosphate rocks originating from different districts around the world.

## 5. CONCLUSIONS

The XRF and ICP-MS results obtained for the phosphate rocks from the El-Sibaiya and El-Hamrawein revealed the presence of thirteen oxides and twenty-five elements (heavy metals, rare earth and trace elements, natural radionuclides). The phosphate rocks have a reduced share of the elements, indicating a decreased transmission of toxics to nature. According to the elemental distribution found in phosphate rocks in the study area in relation to their parent sediments and location, it is quite clear that the changes in phosphate composition depend on the nature of the parent sediments from which the parent rocks are derived. The information acquired in this paper will serve as a reference value and a gauge for the development of an ecological guide for the Egyptian mines of El-Sibaiya and El-Hamrawein.

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