

Geochemistry, Mineralogy and Petrography of Al-Hisa Phosphate Rocks and Its Upgraded Ores

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Abstract

Several samples from phosphate rock and upgraded ores collected from Al-Hisa mine central Jordan were investigated geochemically and mineralogical. Mineralogical study showed that the main mineral phases are Françoise, beside calcite, gypsum clay and silica. The petrography of francolite shows that it is presented mainly in the form of pellets, ooliths and bioclsts, the matrix formed mainly from calcite, micro-quartz and anhydrite. The upgrading process causes enrichment of Françoise, clay and gypsum to some extent, and depletion of calcite and quartz. Thus the TCP increased from 52% in the original phosphate rocks and reaches 64% in the upgraded ores. The dramatic drop of chlorine in upgrading ores reflects its solubility if the effluent water, that might cause increase of Cl in surface water bodies.

Keywords: Phosphate, Upper Cretaceous, Upgraded ores, Francolite, TCP, Jordan

1. Introduction

Jordan has huge reserves of phosphate deposits, the main deposits existed in the southern region of the country (Bender, 1974; Khaled and Abed 1980). The mining industry of phosphate ores consumes up to 6 million m³/year produced from Al-Abyad and El-Hisa mines alone (Jiries et al. 2004). Sadaqa et al. (2001) have studied the depositional environment of the phosphate ore all over Jordan using the ¹⁴C and ¹⁸O isotopes, indicates the autogenic origin for all the phosphates of Jordan, and evidence for active upwelling. In general the concentrations of trace elements such as U, V, Cd, Cr, and As are increasing from south to north, for example, U ranged from 40–60 to 70–80 mg/kg)1 for samples from Esh-Shidyia and Al-Hisa mines, respectively (Jordanian Phosphate Mines Company (JPMC) 1998; Khaled et al. 1990). At Al-Hisa mine U is found in one layer with an average of 100 mg/kg) (Beerbaum 1977). Abed (1982) found that the U concentration increases towards the north as the sediments become more marine facies. Ghosheh and Dodeen (1993) showed that other heavy metals and toxic elements in the Jordanian phosphate rocks are lower compared with several phosphate deposits from the world. Moreover, similar conclusion was reached by Al-Haiti et al. (2001). Jiries et al. (2004) studied the hydro-chemical and isotopic characteristics of the effluent water of both mines. They also reported that quality of the effluent water from Al-Hisa mine was better than that of the Al-Abyad mine, as it shows much lower electrical conductivity (EC) values, which they attributed to the slight difference in ore geochemical properties. Abed et al. 2008; found that potential toxic metals behaves as P and are enriched by a factor of more than 1.5 in the diammonium phosphate (DAP) compared with the input phosphorite. And that the trace metal content in the phosphogypsum is very low. U sticks to the mineral Françoise during upgrading of the ores, and behaves similar to Ca and P₂O₅ (Abed 2011).

The phosphate industry is one of the most contaminating sources to the environment, which contributes to soil, water and air pollution (Vandenhove 2002; Jiries et al. 2004).Hamaiedah and El-Hasan (2011), has found phosphate mines at Al-Hisa is heavily affecting the particulate matter in the areas around the mines. Al-Hwiti et al. 2016; investigated the potential environmental associated with the effluent mine waste water from the Eshidiya mine, the values of conductivity (EC) and sodium adsorption ratio (SAR) indicates that most of the samples are categorized as C₄S₁–C₄S₂. And this water falls into the FAO “slight to moderate restriction on use” category for irrigation.

The objective of this study is to clarify the geochemical, mineralogical and petrographic characteristics of Al-Hisa phosphate ores, and to further investigate the characteristics of the phophogypsum generated from these ores at phosphoric acid plant at Aqaba.

2- Sampling and Analytical methodology

Several hand specimen sized rock samples were collected from Al Hisa Mine in the central part of Jordan as shown in Figure1. The number of samples is 3 and they were labeled as Hisa-1, Hisa-2 and Hisa-3. Two other samples collected from the upgraded phosphate raw material, these samples labeled as Ph-1 and Ph-2, which were collected from the phosphate raw material that used by JPMC-IND COMPLEX in Aqaba. The mineralogical, petrography and chemical studies were performed to all of them.

Several chemical analyses were carried out on the collected samples, these including X- Ray Fluorescence (XRF) (PHILIPS 2400) with an attached 72-position sample changer. Pellets were made by fusing 0.8 g of sample powder and 7.2 g of L2B4O7 in Au/Pt crucible using a flexor machine (Leco 2000) for 3-4 minutes at 1200°C. Which used for analyzing the major oxides and trace elements that present in the phosphate samples. Calcimeter has been employed to identify the calcite content in the investigated phosphate ore samples; in addition to that the

loss of ignition has been examined for the three mentioned samples at 900 °C. Moreover, Fisher assay was utilized to identify the organic carbon content. And X-Ray Diffraction (X-Ray Diffraction system (Siemens D5000 powder diffractometer with Cu-K α -radiation source) equipped with a secondary graphite monochromator (40-position sample stage). The samples were scanned between 10° and 70° 2 θ , using Ni-filtered Cu-K α -radiation (40 kV, 40 mA), divergent and scattering slits of 0.02 mm, a receiving slit of 0.15 mm with stepping of 0.01 mm and scanning speed of 3°/min. The XRD analysis was carried out at the Institute of Geosciences, University of Erlangen-Nuremberg, UK. This machine was employed to identify the major and trace mineral components of some collected phosphate ore samples. Three thin sections were prepared from the Al-Hisa sample for microscopic examination. Nikon polarized microscope with a digital microscopic camera have been employed for the petrography and mineralogical studies.

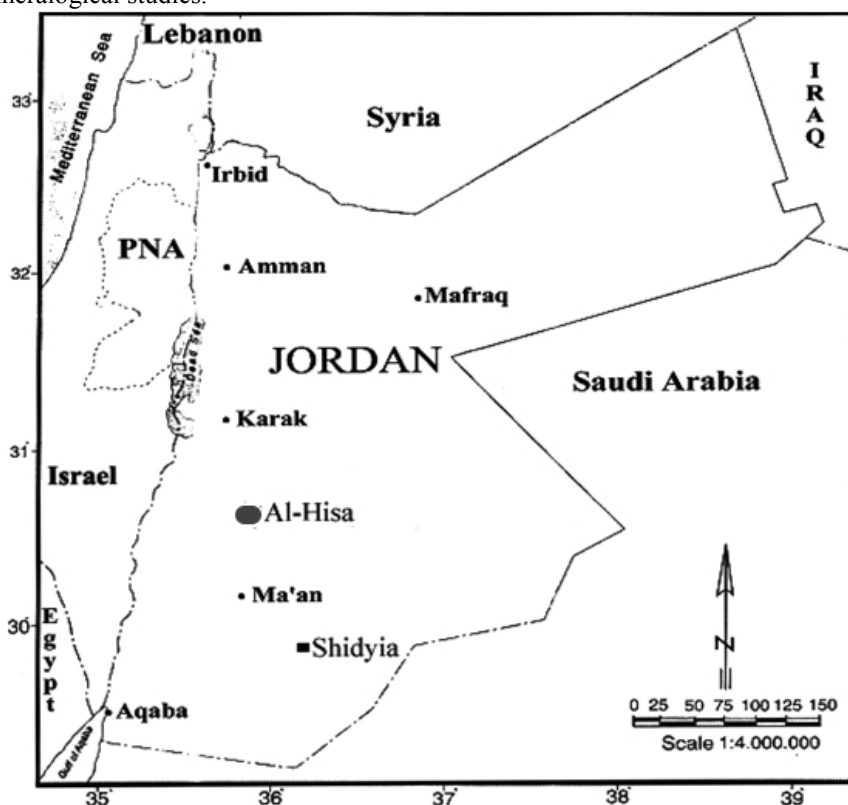


Fig. 2. Map showing the location of AL-Hisa mine

3. Results & Discussion:

3.1 Geochemical characteristics of Al-Hisa phosphate rocks and upgraded ores

Several representative samples collected from the phosphate raw materials that used in Industry Complex for producing phosphoric acid, these samples were numbered as Ph-1, Ph-2. In addition to a rock phosphate ore sample has been collected from Al Hisa Mine namely Hisa-1, Hisa-2 and Hisa-3. All these samples were analyzed by XRF to estimate their chemical composition, and the results are shown in Tables 1&2.

The results obtained from the XRF for the upgraded powdered samples show no significant differences in the major chemical components relating to the small variation in the apatite, calcite and quartz minerals content of the powdered samples. The P₂O₅ content of these samples, as seen from the XRF analysis, ranges between 28.5 to 30.16%, averaging 29.33%. The CaO content ranges between 48.10 to 49.13 %, averaging 48.62. The CO₂ results obtained show that there is a considerable quantity of calcite and François minerals in the analyzed phosphate ore samples, CO₂ was 6.52 in both samples. Fluoride element was detected in a considerable amount which gave an indication on the presence of apatite mineral in the analyzed ore samples, because both of them are usually associated with each other in the nature. According to the XRF analysis that carried out on the Jordanian Phosphate (upgraded samples) for F element, the results obtained show that it ranges between 3.90 to 4.00%, averaging 3.95%. Other detected oxide elements are Al₂O₃, SO₃, SiO₂ and MgO; these oxides are present due to the presence of cryptocrystalline quartz (chalcedony), gypsum and clay minerals in phosphate rock sample.

The analysis of the hard phosphate rock sample which is not upgraded show that P₂O₅ and CaO lower in contents than the previous upgraded samples, while SiO₂ and Cl contents are much higher as seen in Table 1.

Table 1: Results obtained from XRF for major oxides in the phosphate ore samples and upgraded ore samples.

Oxides	Sample Identification				
	Ph-1	Ph-2	Hisa-1	Hisa-2	Hisa-3
P ₂ O ₅	30.16	28.5	24.0	23.8	24.2
CaO	49.13	48.1	44.2	44.02	44.1
SiO ₂	7.61	9.00	16.6	15.7	17.7
MgO	0.35	0.366	0.21	0.20	0.31
Al ₂ O ₃	0.527	0.823	0.32	0.33	0.30
Fe ₂ O ₃	0.255	0.385	0.37	0.32	0.41
Na ₂ O	0.6	0.575	0.8	0.76	0.88
K ₂ O	0.031	0.00	0.05	0.05	0.06
SO ₃	1.23	1.28	0.83	0.86	0.82
TiO ₂	0.008	0.03	0.013	0.014	0.017
MnO	0.015	0.0105	0.008	0.006	0.009
CO ₂	6.52	6.52	9.58	9.44	9.67
F %	3.90	4.00	2.58	2.62	2.49
L.O.I	8.15	9.47	9.50	9.61	9.47

Table 2: XRF results for trace elements concentrations in phosphate ore samples and upgraded samples.(ppm)

Trace Elements	Sample Identification					Standard Error
	Ph-1	Ph-2	Hisa-1	Hisa-2	Hisa-3	
Cl	718	1123	4893	4670	4915	0.0059
Zn	159	199	101	109	89	0.0031
Cr	118	96	9.0	9	8	0.0023
V	75	51	79	73	80	0.0015
U	62	62	81	65	88	0.0007
Y	50	68	49	47	54	0.0005
Zr	28	55	48	44	43	0.0006
Ni	22	11	7	7	9	0.0004
Cu	17	26	24	28	25	0.0004
Sr	1160	1314	1036	995	1110	0.0190

3.2 Mineralogy and petrography of Al-Hisa phosphate rocks and upgraded ores

3.2.1 Mineralogical results

The mineral identification was carried out on the collected samples. The main methods for identification the mineral components of the phosphate ore samples is the XRF method to calculate the percentage of minerals in the phosphate ore samples. Calcimeter was employed to determine the amount of calcite content in the ore samples and powder X-Ray diffraction used to identify the major and trace minerals component of the phosphate ore and upgraded samples.

Sedimentary Jordanian phosphates are mostly composed of varieties of apatite Ca₅(PO₄)₃(OH, Cl, F), mainly in the form of François pellets (carbonate-fluorapatite) Ca₅(PO₄.CO₃)₃F with molecular weight equal to 486.82gm. Dahllite apatite mineral (carbonate hydroxylapatite) was found in lesser extent. This was evidenced by the X.R.D results of the analyzed phosphate ore samples revealed that the main apatite mineral is fluorapatite type as revealed in Figure 2.

Table 4: Showing the Calculated minerals that depending on the XRF analysis that obtained in Table 1.

Mineral %	Upgraded ore sample	Rock sample
Francolite	80.45	65.84
Calcite	6.56	15.01
Gypsum	2.22	1.78
Clay	3.44	1.60
Cryptocrystalline quartz	6.30	15.78

Depending on the obtained concentration of P_2O_5 , the Tri-calcium Phosphate TCP was calculated using the equation $TCP = P_2O_5 * 2.185$ (Momani, 2011), then values of TCP are listed in Table 5.

Table 5: Showing the Calculated Tri-Calcium Phosphate (TCP) depending on the XRF analysis that obtained from XRF

Sample Identification	Tri-calcium phosphate (TCP) $Ca_3(P_2O_4)_2$
Upgraded ore sample	64.14
Rock sample	52.44

3.2.2 Petrography results

The main components of phosphate rock as seen in thin sections are:

1. Phosphate pellets: They are composed of collophane (cryptocrystalline apatite) with grain size ranges between 0.5 to 5.2 mm; vary in shape from spherical to ovoidal and very well-sorted. Under the plane polarized light (PPL), their color ranges from light brown, yellowish brown to black. The black colors may be due to presence of organic matter inclusions and indicative of formation under reducing conditions Figure3.

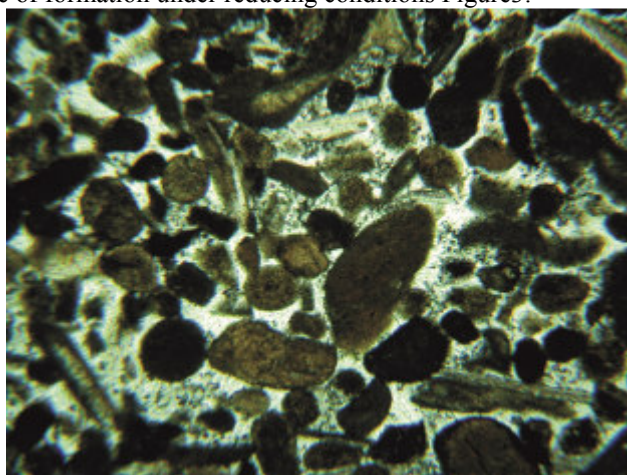


Fig 3 Anisotropic phosphate collophane (rounded pellets), ppl. Mag. 4x

2. Under crossed polarized light (XPL) the phosphate pellets are isotropic and showing a very weak birefringence (dark colors) so, it was too difficult to see any internal structures that may be present in the grains of phosphate Figure 4.

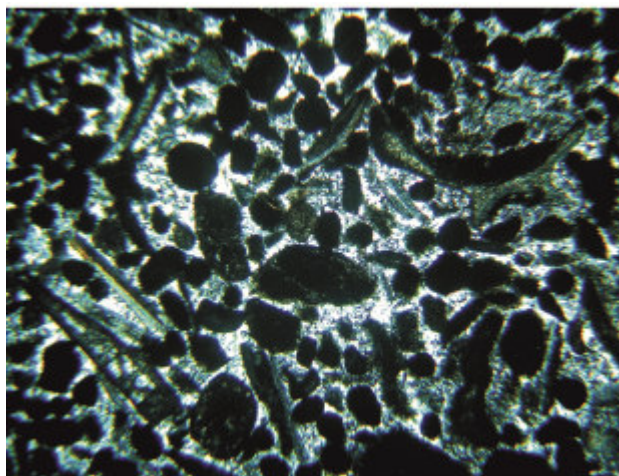


Fig 4 Isotropic phosphate collophane (rounded pellets), xpl. Mag. 4x

3. Phosphate ooliths: These grains show a well-defined concentric structure with some times a nuclei occurred in the centers of the phosphate grains. They are usually consisting of collophane alternating with Françoisé laminate Figure 5.

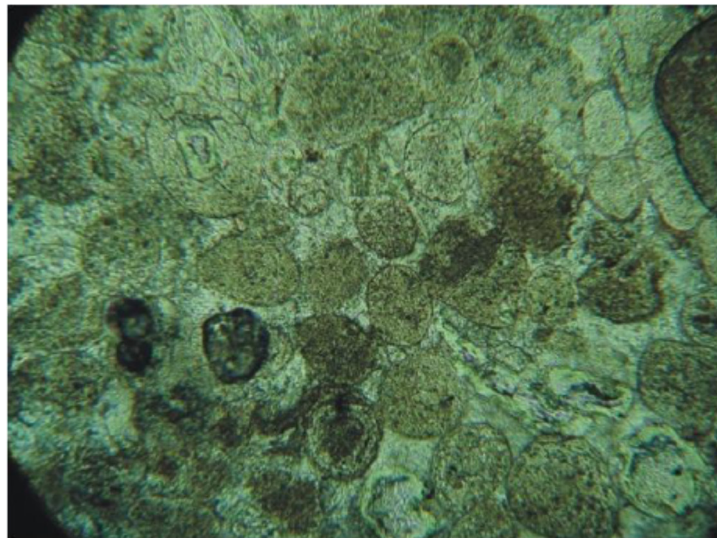


Fig 5 Anisotropic rounded pellets with concentric texture, ppl. Mag. 4x

3. Phosphate nodules (intraclasts): They are large grains formed in the sea-floor, circular to elliptical shape. They are described as a coated bioclasts, comprises of nucleus (bioclasts) surrounded by a coating of micrite which makes a sharp contact with the internal materials. The coating is not laminated.

4. Bioclasts (skeletal particles): They are the remains, complete or fragmented of hard parts of carbonate or apatite-secreting organism. Anisotropic phosphate (apatite), occur as teeth and bone fragments, forms about 20%. Some of bone fragments have shown an internal structure filled with a fine phosphate material Figure 6.

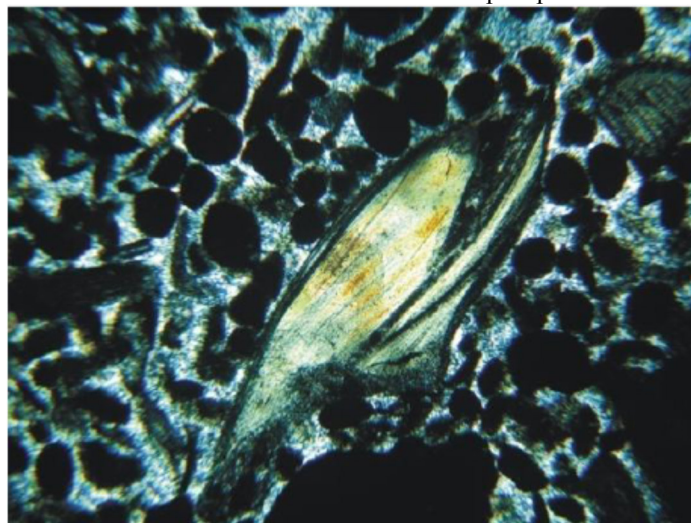


Fig 6 Isotropic collophane pellets with teeth fragments, xpl. Mag. 4x

1. Cement Materials: The main cement material that surrounding the phosphate components was spray calcite forms more than 20% in some views Figure 7.

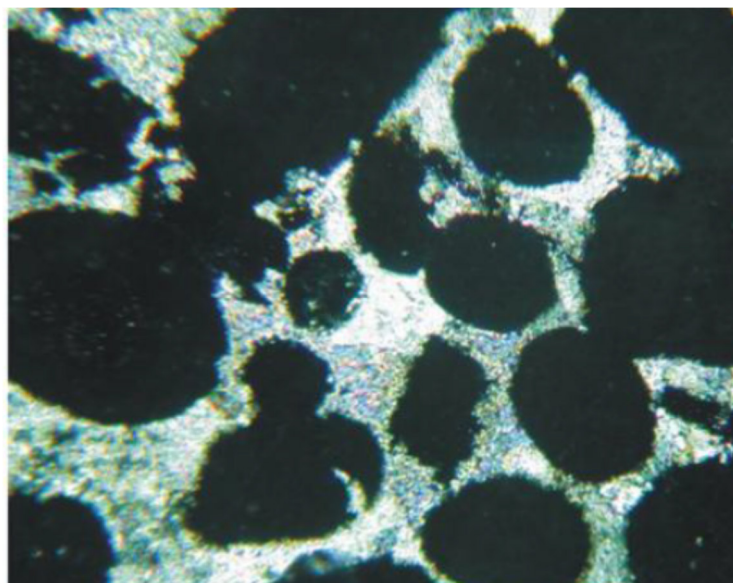


Fig 7 Calcite cementing material surrounding dark collophane pellets, xpl. Mag 4x
The other cement material present in the phosphate rock is anhydrite but occur as a minor content (< 3.0%).

1. Matrix Material: Many of the phosphate grains are set in a matrix of micro-quartz (chert) forms more than 20% in some views Fig 8. The grain packing clearly indicates that the chert represents an original matrix.

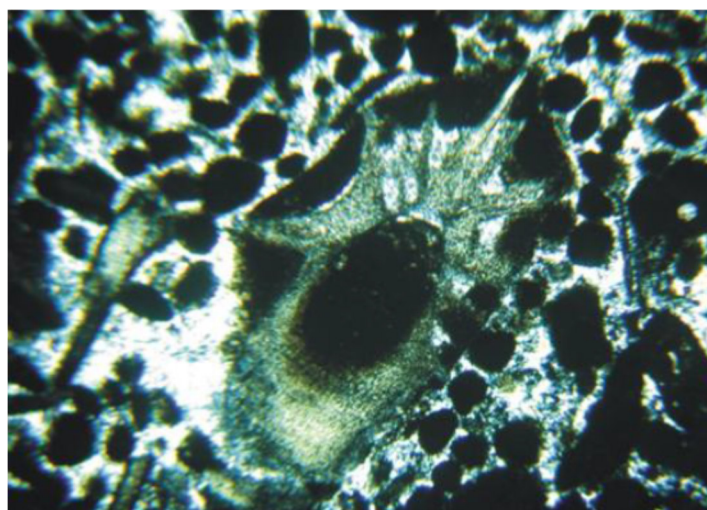


Fig 8 Cryptocrystalline silica matrix surrounding the dark collophane pellets. Xpl. Mag. 4x
The textures of phosphate rock is the grain-stone texture according to Dunham classification (1962). Where the rock is grain-supported with a spar calcite cement and cryptocrystalline quartz matrix.

Conclusions

The Jordanian phosphate ore deposits at Al-Hisa area that belongs to the Upper Cretaceous rocks, were mined commercially since 70's of the last century. The studies indicated ore reserves of 2000 million tones with an average P_2O_5 content of 30%. In the upgraded ore large quantities of Calcite, Clay and Silica were removed through washing with fresh water. The results upgraded ore have Fra \tilde{c} oise increased from 65.84 up to 80.45%, Tri-Calcium Phosphate (TCP) $Ca_3 (P_2O_4)_2$ is also increased from 52.44 up to 64.14. Beside that few trace elements such as Zn and Cr get enriched in the upgraded ores, while Cl is very high in the original rocks.

The mineralogy and petrography studies revealed that the most abundant mineral in the upgraded phosphate ore samples was Fra \tilde{c} oise, that found in many forms as pellets, ooliths and bioslasts, the cementing materials are spray calcite, micro-quartz and the anhydrite.

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