NEW PHOSPHORITE DEPOSITS IN NAQIB ETAIQ AREA (SOUTHEASTERN JORDAN)

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ABSTRACT. The study area situated to the southeast of Esh-Shidiya mines in the southeastern part of Jordan close to the Saudi Arabia borders. The phosphorites of Naqib Etaiq area (Campanian-Maastrichtian in age), crops out along the southeastern extension of Ras En Naqab-Batn Al Ghul escarpment, are up to 26 m thick and unconformably overlies the Upper Cretaceous-Batn Al Ghul Group. The phosphorites at this locality are composed of predominantly phosphatic sand, sandstone, phosphate, interbedded with thin limestone beds, coquinal limestone, coquina, marl, phosphatic chert and chert. The phosphate sequence in the study area shows lateral variations in lithology, thickness and distribution of the phosphate beds. Generally, phosphates at these localities form approximately 50% of the section and occur as beds, up to 1.7 m thick. Field observations indicate the presence of fragmented bones, reptile carapaces, Thalassinoides, gastropods, bivalves. Chemical analyses indicate that P_2O_5 is up to 42.13%. The results of X-ray diffraction analyses indicate that the main phosphatic mineral is carbonate fluorapatite (francolite). Preliminary petrographic studies indicate the presence of phosphate pellets, bone fragments, intraclasts, fish teeth, and quartz grains cemented by calcite and dolomite. The phosphorites in the study area were probably deposited in marine environment, upper shoreface, very close to the shore lines of the continent.

НОВИ ФОСФОРИТОВИ НАХОДИЩА В ОБЛАСТТА НАКИБ ЕТАИК (ЮГОИЗТОЧНА ЙОРДАНИЯ) Халед Таравнех

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РЕЗЮМЕ. Изучаваният район е локализиран югоизточно от мините Еш-Шидия в югоизточна Йордания, близо до границата със Саудитска Арабия. Фосфоритите от областта Накиб Етаик (с кампан-маастрихтска възраст) се разкриват в югоизточното удължение на откоса Рас Ен Накаб-Батн Ал Гул, като са с мощност 26 m и залягащи съгласно върху горнокредната група Батн Ал Гул. Фосфоритите в този район са представени главно от фосфатен пясък, пясъчник, фосфатни лещи във варовикови гназда, кохинален варовик, мергели, фосфатен кремък и кремък. Фосфатната последователност в разреза показва латерална вариация в литология, дебелина и разпределение на фосфатите гнезда. Обикновено фосфатите в тези находица заемат до 50% от разреза и се явяват във вид на гнезда с можност до 1.7 m. Полевите наблюдения показват индикации за присъствие на фрагментирани кости, части от рептилии, таласиноиди, гастроподи и бивалвии. Химичният анализ показва, че съдържанието на P₂O₅ във фосфатните гнезда се увеличава нагоре в разреза и варира от 8.0 до 26.42%, като чрез СЕМ в избрани места с фосфати. Предварителни петрографски изследвания индикират присъствието на фосфатни показват, че главният фосфатен минерал е флуорапатит (франколит). Предварителни петрографски изследвания индикират присъствието на фосфатни палети, костени фрагменти, зъби от риби и кварцови зърна споени от калцит и доломит. Фосфоритите от изучавания район са вероятно отложени в морска обстановка, в горната част в непосредствена близост на континенталната брегова линия.

Introduction

Phosphorite deposits in Jordan form an important part of the Upper Cretaceous-Eocene Tethyn Phosphorite Belt stretching from Morocco to Turkey, Syria, Iraq, Saudi Arabia and Palestine (Klemme, 1958, Sheldon, 1964, Notholt et al., 1989). The Jordanian phosphorites were deposited in the transitional zone between a stable shelf in the south and the Tethys Sea in the north Jordan due to the upwelling currents Bender (1974). Economic phosphorite deposits are present in the areas of Rusiefa, Qatrana, Al Abyad, Al Hasa and Esh-Shidiya. Economic phosphorite deposits were discovered also by Mikbel and Abed (1985) in northwest Jordan. Details for the Jordanian phosphorite deposits are found in Reeves and Saadi (1971), Khalid (1980), Khalid and Abed (1982), Abed and Khalid (1985), Al-Agha (1985), Abed and Al-Agha (1989), Abed and Fakhouri (1990, 1996), Abed et al (1992), Tarawneh (1997) and Tarawneh and Moumani, 2005). Most of these works discussed many subjects of geology, mineralogy, chemistry and genesis of these deposits.

This is the first detailed study of the phosphorite deposits of the areas of Naqib Etaiq in southeastern Jordan (Fig. 1). The aim of this research is to study the geology, mineralogy, chemistry and the genesis of this newly discovered phosphate.

Geological setting

The phosphorites in the study area crop out in the south part of Jordan along the southeastern extension of Ras En Naqab escarpment (Jibal Kabid and Abu Mil areas), and situated to the southeast of Esh Shidiya mines; close to the Saudi Arabia border (Fig. 1).

The phosphorite deposits of Naqib Etaiq area are up to 26m thick (Fig. 2) and rests unconformably on the Upper Cretaceous-Batn Al Ghul Group and the Lower part of Belqa Group (undifferentiated). The phosphorite section is found in the phosphorite member of Bender (1974), the topmost of Amman Formation of Masri (1963), early Maastrichtian in age

(Burdon, 1959; Hamam, 1977; Abed and Ashour, 1987; Glenn and Arthur, 1990). It is adopted by the National Geological Mapping Project/ NRA to Al Hisa Phosphorite Formation (AHP) (Campanian-Maastrichtian).

The Phosphorite sequence in the study area shows lateral and vertical variations in lithology, thickness, distribution of phosphorite beds (up to 1.7m thick), in addition to the variation of P₂O₅ content. Generally, phosphates form approximately 50% of the sequence. Field observations indicate the presence of bone fragments, reptile carapaces, and different types of fish teeth (pycnodont and mosausurus tooth; probably of crocodile) intensively occur in the friable phosphatic sand of the lower part of the sequence. The phosphorites occur as several levels increasing upward and intercalated between multiple event within coarse grained quartz sand, sandstone, limestone, coquinal limestone, chert, phosphatic chert, marl and chalky limestone. The coarse-grained quartz or granular sandy phosphate occurs in the basal and in the middle parts of the sequence. Generally, the contacts between phosphatic beds and the lithologies between them are usually gradational.



Fig. 1. Location map

Petrography

Representative samples from the study area were thin sectioned. In general, the Jordanian phosphates made up of four types of phosphatic particles as follows: pellets, intraclasts, skeletal fragments and coated grains (Abed and Al-Agha, 1989; Khalid and Abed, 1982; Abed and Fakhouri, 1996). The composition of the study phosphate is similar to the other Jordanian phosphates, with small differences of the amount of the phosphatic particles.

As a rule grains constitute most of the phosphatic part of the study phosphorites. The matrix is being usually silicic and locally calcitic. Clay and phosphatic matrix also occur. The main diagenitic replacements of the Naqib Etaiq phosphate particles are silicification and partly calcitization. Silicification of phosphate particles has previously been reported by Kolodny (1969) from the northern Neqev phosphorite.



Fig. 2. Graphic log of the phosphorite section

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Among the phosphatic grains, pellets are the most common and characteristic component, particularly in the high-grade phosphorites. These pellets are structureless, rounded to subrounded with smooth boundaries (0.060-0.5 mm in diameter grains). Their X-ray pattern is always that of francolite (Soudry and Nathan, 1980). In the Jordanian phosphorites these particles might be fecal in origin (Abed and Fakhouri, 1996). Intraclasts are common in the study phosphorites. They have irregular form (up to 1cm in diameter) and have an internal structure. Some of these intraclasts are composed of translucent, slightly microcrystalline apatite. Intraclasts may include other particles as pellets or fragmented bioclasts and quartz, therefore these intraclasts are good indicators for reworking (Khalid, 1980). Skeletal fragments include bones and teeth of various size (1 mm - 2 cm in diameter. They made an important component of the phosphatic grains and concentrated in the lowermost part of the sandy phosphatic beds and in the friable sand at the basal part of the sequence. Petrographically, they composed of microcrystalline apatite with prismatic shards and sharp edges, and many of them show a relict organic structure. Some of the skeletal fragments are replaced by microguartz, indicated silicification of these fragments. Coated grains and aggregates are present. They are generally larger than 0.25 mm. They are made of cryptocrystalline apatite at the center and crystalline apatite as a rim around them.

Detrital quartz is abundant in the studied samples. The grains are rounded, subrounded to subangular with various sizes. It occurs as siliceous matrix, usually very fine-grained quartz or coarser grains with irregular shape.

Mineralogy and chemistry results

Phosphate rocks are mostly composed of varieties of apatite. They include fluorapatite, carbonate flourapatite (francolite), carbonate hydroxylapatite (dahlite) and chlourapatite. X-ray diffraction indicate that the apatite mineral is francolite.

Representative phoshporite samples were analysed and the results are shown in Table 1. In general the studied phosphorites relative to the Upper Cretaceous phosphorite horizons in central and northern parts of Jordan are richer in SiO₂ and poorer in CaO, while the P₂O₅ has a wide range. Relationship between the study phosphate and the closer Esh Shidiya Mine have been done with aim to see the similarity and differences in chemical composition between these localities. Graphic illustrations between P2O5 from one side with other chemical components are shown in Fig 3. The average content of SiO₂ is 29.91%, whereas in the Esh-Shidiya phosphate it is 18.72% (Khalid, 1980). In the studied samples the SiO₂ is mainly present as detrital quartz and clay minerals or occur as silica in the form of chalcedony. Silicon can partly replace phosphorous in the apatite lattice (Cathcart and Gulbrandsen, 1973).

The CaO content ranges between 12.74-41.76%, whereas in Esh-Shidiya phosphate is between 27.87-50.63% (Khalid, 1980). Chemical analyses and microscopic investigations indicate that the major part of the carbonates is made of sparitic to microsparitic calcite, whereas dolomite is only present in a few samples in the dolomitic sandy phosphate bed.

The P_2O_5 content ranges from 8.0 to 26.42%, whereas in Esh Shidiya mine it ranges between 5.83-33.96% (Khalid, 1980). This wide range of P_2O_5 in the studied samples is mainly due to the admixture of non-phosphatic minerals such as quartz, calcite and dolomite. In the apatite lattice PO₄-group may be partly replaced by OH-group (McConnell, 1965). Phosphorous may be partly replaced by the following elements As, V, Si, S, C and Cr (Cathcart and Gulbrandsen, 1973), whereas calcium can be partly replaced by Na, Sr, Ba, Cd, Rb, Re, Th and U (McConnell, 1973).

The positive correlation is clear between P_2O_5 and F, which indicate that the major phosphate mineral is francolite. The relationships between P_2O_5 with CaO, CO₂ and SiO2 are randomly orientated.

The MgO content in the studied samples ranges between 0.13 to 2.34, whereas in Esh-Shidiya phosphates is around 0.66% (Khalid, 1980). The MgO is associated with dolomite, apatite, calcite and clay minerals. Mg can replace Ca in

apatite and calcite lattice, but in the studied samples there is a negative correlation between P_2O_5 and MgO due to the low content of MgO in the studied samples.

The CO₂ content ranges between 1.28-18.29%, whereas in Esh-Shidiya Mine is about 7.29%. McConnell (1973) considered that the CO₃ ions partly substitute PO₄ ions. In the studied samples, CO₂ is mainly present in the carbonate and phosphate facies. However, because the type of apatite is francolite it should be part of CO₂ incorporated in the apatite lattice. This point indicated because the petrographic study shows a little amount of organic matter present in some fecal pellets and in the groundmass. The SO₃ content ranges between 0.10-1.87%, whereas in Esh-Shidiya phosphates is around 1.06% (Khalid, 1980). The (PO₄) group in the apatite can be also replaced by SO₄ (Stowasser, 1975). In the studied samples sulphur may occur in the apatite structure as a normal constituent of phosphate lattice or as gypsum which was detected by X-ray diffraction in this study.

The fluor content ranges between 0.85-2.34%, whereas in Esh-Shidiya Mine is around 3.06% (Khalid, 1980). Flour is present in the apatite lattice and it occurs free or associated with (OH) and O-ions (McConnel, 1973). In the studied samples the F correlates positively with P_2O_5 . The chlorine content in the studied samples varies from 0.04 to 1.31%, whereas in Esh Shidiya phosphates the Cl is around 0.061% (Khalid, 1980). In the phosphates, chlorine may be present in the apatite lattice where it may replace F or OH group (Blatt, *et al.*, 1972). There is no clear relationship between Cl and P_2O_5 in the discussed samples, therefore most of the Cl should be associated with clay minerals, or partly incorporated in the apatite structure replacing F.

Scanning Electron Microscope (SEM), Back Scattered Image (BSE) and Secondary Electron Image (SEI) was used to identify the phosphate minerals and to get more details about chemical composition of the studied phosphate. For this purpose phosphate areas in thin sections were analyzed. The results of chemical composition of major and minor elements are shown in Table 2. The results of SEM indicate that the groundmass of the studied phosphates consist of microcrystalline apatite that form the structure of pellets, fish teeth, bone fragments and other unidentified phosphate fragments. The apatite occur as dark envelops surrounding light cores of these fragments. The results of SEM analyses in different phosphate areas (cement, core and rim of pellets, fish teeth and bone fragments) indicate that the P_2O_5 content varies from 39.25 to 42.13 %, whereas the fluor ranges between 3.28 and 4.21%. The content of other oxides associating the apatite is shown in Table 2.

SEM analyses confirm that the phosphate facies is mostly made up of P, Ca, F, Cl, Si and Na, that are involved in the apatite lattice. Replacement of P by Si, Ca by Na and F by Cl is more common in similar phosphates (Cheny et al., 1979). Graphical illustrations showed the relationships between P_2O_5 versus CaO, CO₂ and F (Fig. 3). Results of SEM indicate also that there is some kind of positive relationship between P_2O_5 with other oxides associating the apatite lattice. F/P2O5 value ranges from 0.04 to 0.10, while CaO/P2O5 value ranges from 1.23 to 1.38. Such values are similar to the values of composition of francolite (Cheney et al., 1979).

No	MaO	Al-O-	SiO	D.O.	6-0	FacOs	<u> </u>	<u> </u>	Е	CI		Total
_	ivigO	AI2U3	3102	F2U5	CaU	Fe2O3	002	303	Г	U U	F/F2U5	TOLAI
1	0.76	0.05	33.23	23.56	27.18	0.33	13.56	0.1	0.85	0.08	0.036	99.72
2	0.45	0.01	59.03	13.51	18.24	0.23	6.5	0.13	1.25	0.09	0.092	99.53
3	0.32	0.07	69.94	8.52	12.74	0.44	5.32	0.36	1.32	0.65	0.15	99.83
4	1.26	0.02	8.07	24.69	43.22	0.19	19.26	0.72	1.02	0.04	0.04	98.5
5	14.7	0.05	6.98	8.00	49.55	0	18.23	1.31	1.21	0.4	0.15	100.58
6	1.86	0.21	23.14	20.82	46.88	0.88	2.35	0.97	1.12	0.89	0.05	99.27
7	0.58	0.97	24.23	24.15	42.94	0.89	3.21	0.48	1.68	0.82	0.06	100.1
8	0.7	0.01	39.4	16.58	34.56	0.33	5.25	1.28	1.01	1.3	0.06	100.52
9	2.34	0	33.85	15.71	36.31	0.26	7.75	1.87	0.87	0.04	0.05	99.05
10	0.61	0.07	33.25	18.92	36.65	0.89	4.54	2.23	2.34	0.7	0.12	100.35
11	0.9	0.11	18.66	24.09	45.3	0.5	6.23	0.95	2.11	1.31	0.08	100.26
12	0.13	0	29.08	20.35	39.88	0.26	6.89	0.83	1.7	0.87	0.08	100.07
13	1.89	0	15.5	26.42	45.67	0.71	5.23	1.12	2.1	1.01	0.07	99.75

Table 1Chemical analysis of the phosphate samples from the studied area

Table 2
Chemical composition of the various types of phosphate samples in percent using SEM

Sample								
No	CaO	P ₂ O ₅	SiO ₂	Na ₂ O	F	Total	F/P ₂ O ₅	CaO/P ₂ O ₅
1	51.1	41.67	1.32	0.88	4.21	99.18	0.10	1.22
2	48.5	42.13	1.9	1.04	3.56	97.13	0.08	1.15
3	49.39	41.42	3.5	0.89	3.28	98.48	0.07	1.19
4	52.3	40.2	2	1.18	3.36	99.04	0.08	1.30
5	51.12	41.3	1.1	1.8	3.54	98.86	0.08	1.23
6	54.2	39.25	1.5	1.21	3.26	99.42	0.08	1.38
7	50.7	41.1	2.1	1.1	3.62	98.62	0.08	1.23
8	49.8	39.8	2.25	1.9	3.91	97.66	0.09	1.25
9	51.95	40.01	1.95	1.65	3.56	99.12	0.08	1.29
10	48.54	37.77	1.23	0.98	2.56	91.8	0.06	1.28
11	49.23	36.98	2.23	1.23	2.98	91.08	0.08	1.33
12	50.23	38.47	2.24	1.33	1.58	93.85	0.04	1.30
13	49.33	39.55	1.89	0.88	1.98	93.63	0.05	1.24
14	47.89	37.88	1.11	0.94	2.11	89.93	0.05	1.26
15	49.87	40.22	2.12	1.25	3.25	96.71	0.08	1.23





Fig. 3. Graphical representation of the XRF and SEM analysis between P_2O_5 versus other chemical components

Genesis

The rate of deposition, sedimentary structures, composition and thickness of the phosphorite deposits in the study area are closely controlled by the local palaeostructural relief.

The study phosphate is of grainstone type. Such type of phosphate in ancient strata are commonly viewed largely as a reworked product of synsedimentary phosphatized mud generated in low-energy and organic rich marine environments (Cook, 1970, Rigges, 1979, Glenn and Arthur, 1990). The processing of washing and transport would concentrate the phosphorite particles "Pellets" generated later as phosphorite beds within tectonic troughs in near shore setting (Soudry, 1992). Therefore, such phosphates could be formed not due to single factor, but due to series of successive processes providing a final concentration of phosphorus (Baturin and Bezrkovis, 1979). These processes include winnowing of light and fine non-phosphatic fractions and residual concentration of coarser material, including phosphorite grains (Soudry and Nathan, 1980). The granular phosphorites of both southeastern Jordan and Negev (Soudry and Lewy, 1988) are essentially grainstones, which are extremely porous and are situated near-surface in an arid area. The environment of deposition and early diagenetic processes are apparently reflected in the fabrics and grain composition in such phosphate. The bioturbation features commonly associated with the granular phosphorite, and the high energy of character of these rocks, point to deposition in arid environments with good mixing of waters that have chemical composition typical to sea-water (Nathan et al., 1990). It can be assumed that the presence of fauna in addition to the higher amounts of siliciclastics in this sequence indicate that the phosphorites in the study area were probably deposited in marine environment: upper shoreface. very close to the shore lines of the continent.

Conclusions and recommendation

- The phosphorite horizons in the study area differ from phosphorite horizons in northern and central Jordan by their high content of silica.
- 2. The P_2O_5 content has a wide range (8.0-26.42%) and increasing upward in the measured section, whereas through SEM analyses it is up to 42.13%.
- 3. Petrographically, the study phosphate characterized by uniform composition consist of microcrystalline apatite

that form pellets, bones, fish teeth and unidentified phosphate fragments.

- 4. X-ray diffraction shows that the major phosphate mineral is francolite (carbonatefluorapatite).
- 5. Further detailed studies on the phosphorites of Naqib Etiaq and around areas are highly recommended in order to establish a regional correlation of lithology, petrography, mineralogy and geochemistry with other phosphate horizons in central and southeastern Jordan, particularly with Esh-Shidiya phosphate.
- Drilling a few boreholes in this area to show the real thickness/distribution and lateral changes of the phosphate horizons and their relationships with Esh-Shidiya phosphates are highly recommended.

Acknowledgements. The author would like to thank Dr. M. Hijazen, present Director General of Natural Resources Authority/Jordan. Thanks are due to Mr. D. Jaser, Director of Geology and Mr. Tarawneh, B. Head of the Geological Mapping Division for their help.

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Geology and Prospecting of Mineral Deposits, Faculty of Geology and Prospecting