Diagenesis of Paleocene phosphatic deposits in Djebel Onk, Algeria

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Abstract
The economically interesting Algerian phosphorite deposits from the Djebel Onk area are of Upper Thanetian (Upper Paleocene) age. They are approximately 30 m thick and thin to the north. Above the main phosphorite thin layers of phosphorite alternate with layers of marl, limestone and dolomite. At Kef es Sennoun, the bottom part is phosphorite, superposed by approximately 50 m Ypressian (Eocene) marl and dolomitic limestone. At the top, Lutetian (Eocene) gypsum has a discordant contact with overlying Tertiary and Quaternary deposits.
Eight thin sections from the Djebel Onk area have been studied. They are all dominated by apatite peloids and ooids, and contain additionally bioclasts, detrital glauconite, feldspar grains, diagenetic alkali feldspar, zeolite, dolomite, calcite and chert.
Based on a comprehensive description of the thin sections, three different groups could be identified.
Based on the petrographic study of the Djebel Onk phosphorite it is possible to distinguished 5 steps to characterize the formation and diagenesis of the deposits.

Introduction
Phosphatic rocks are important economic resources. The Algerian phosphorite deposits from Paleocene and Eocene are part of Tethys phosphatic province, stretching from Morocco in the west through northern Africa and the Middle East though Iraq in the east. Phosphatic rocks were deposited at the southern coasts of Tethys through the late Cretaceous and the early Tertiary, and represents 60% of world phosphatic rocks (Guiraud et al.2005). The diagenetic impact on phosphorite has a significant influence on the economic value of the resource because it may control the amount and distribution of non-phosphate minerals and poisonous trace elements. The phosphates are mainly grainstones of apatite peloides, bioclasts and ooids, and generally have very high porosity. Several studies have been made of the present deposits with relation to production of phosphorus, (for example Merabet et al. 2004) or the chemical composition (for example Bezzi et al. 2001). We have studied the diagenesis of the phosphates to illustrate the timing of introduction of diagenetic minerals. The most important mineral is dolomite which also is also degrading the economic value of the phosphorite. Dolomite occurs in two compositional varieties. Because of their different stability, secondary dissololution of dolomite was locally important. Minor cements are calcite, chert, K-feldspar, and clinoptinolite. Based on the relative timing of mineral formation and dissolution, we could identify 5 steps in the formation of the phosphorite deposit.

Geological setting
The Djebel Onk phosphate basin is located in eastern Algeria, on the Algerian-Tunisian border, approximately 300 km to the South of Annaba City (Fig.1). The geological formations are composed of calcareous rocks of Maastrichtian to

Quaternary age. The phosphatic succession is approximately 30 m thick and thins to the north. It is exposed in the Djebel Onk anticline in the north east of Algeria. It is 3 km wide and 20 km long from east to west. The northern flank has a low slope, typically below 10°. The southern flank has very steep slopes with gradients up to 90°. Djebel Djemi-Djema is located southeast of Djebel Onk as a smaller anticline, (Fig.2). The two anticlines are separated by a 1 km wide syncline filled with Miocene and Quaternary detritrital sediments. Ypressian and Lutetian deposits are discordantly overlain by Miocene deposits because of differential erosion due to regression through the epeirogenic stage in late Eocene. This main phosphatic layer is clearly stratified and is generally subdivided into three sub-layers that are shown in Fig.2.The basal part is dolomitic and grades upwards into phosphorite. The upper part consists of alternating layers of marl, limestone, dolomite and phosphorite, and is overlain by approximately 50m of Ypressian (L. Eocene) marl and dolomitic limestones and Lutetian (M. Eocene) gypsum.

Samples and methods

Eight samples from the Kef Es Sennoun (PNB, E04DP, E10PM, E12PN and E13PM) on the southern flank of the Djebel Onk Anticline, and from Djemi Djema on the southern slope of Djebel Djemi-Djema (E16, E17 and E19), (Fig.2) were selected for petrographic analyses. Optical microscopies, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) were preformed to identify the composition and diagenesis.

Petrography

All studied samples are composed of apatite peloids and ooids, which constitute about 60% of the samples. In addition, samples contain bioclasts, glauconite grains and rounded quartz and alkali feldspar. Diagenetic constituents are dolomite, zeolite, K-feldspar, chert, and calcite. Data are shown in Table.1. The terminology of Johnson et al. (2007) has been applied for phosphatic grains. Based on the petrographic description 3 groups of phosphatites were distinguished.

Peloids

Thin sections contain up to 60% of cream to orange and light brown to dark brown fine to medium peloids. Their outer margin commonly has lighter or darker bands or rims. Many peloids have bioclasts, glauconite, or mineral grain cores (Fig.3).

The surface of most peloids is perfectly smooth with a polished appearance.

The composition of the peloids is almost entirely apatite, but EDAX data demonstrates a very small amount of Si, Al, Mg, and K that probably represents clay minerals.

Ooids and peloids with circular solution structure:

Figure.4 shows an ooid with concentric rings of material with alternating colors and a peloid with radial pattern which is a characteristic for ooids deposited in high energy level environments.

Bioclast

4-15 vol% of the studied phosphorites consist of bioclasts. Common types are fish fragments, algal fragments, and shark teeth (Figs.5) as described by Baioumy et al. (2007). Bioclasts have the same size distribution as other grains. Fish fragments in particular are more elongated than other grains, and such grains are often cracked during compaction.

Glauconite

Glauconite occurs in small amounts (1-5%) in all samples as yellowish-green grains with irregular dark brown areas. It has the same size as the other grains and is generally deformed by compaction.

Quartz

Detrital quartz grains occur in trace amount in several samples. The grains contain numerous small fluid inclusions.

Feldspar

Well-rounded grains of alkali feldspar occur in trace amounts in most.

Silica fossils

Some "ooids"-like particles have circular solution structures (Fig.6). Based on the shape of these structures they are classified as dissolved silica fossils (diatoms or radiolarians) that has been trapped in apatite material.

Diagenetic components

Dolomite

Dolomite is the most important cement. It has hypidiotopic texture with varying degrees of dissolution in different samples (Figs.7). In samples with small amounts of dolomite, the crystals are generally euhedral. Dolomite displays a compositional zonation in SEM-BSC and appears as different grey scale of successive zones. The zonation might be enhanced by selective dissolution of specific zones. EDAX and XRD data indicate the presence of two different compositions, one being almost stoichiometric dolomite, the other being enriched in Ca.

Calcite

Calcite cement locally dominates in sample E04DP. There are also small amounts of calcite in PNB, E10PM and E12PN. In E16 and E19, small veins are filled by calcite (Fig.8). According to EDAX data the calcite is almost pure $CaCO_3$.

Chert

Large amounts chert occurs as microcrystaline matrix (<2-µm) in E12PN and PNB, located in pores between peloids and dolomite crystals, indicate the presence microquartz or of siliceous microfossil types, such as radiolarians and diatoms which their original skeletal material is usually opaline silica (Fig.9). Besides quartz, the chert matrix also contains small amounts of apatite, dolomite and possible clay minerals or zeolite as estimated from from EDAX data, which illustrates the presence of Al, Mg, P, and K.

Zeolite

Zeolite crystals have been observed in two different size orders. In E13PM, PNE12, E17 and E10PM in polarisation microscope and SEM as small rectangular crystals (about 0.05 mm) with internal dissolution, (Fig.10). In E10PM very small crystals (a few µm) has been revealed by SEM-SE. They are located on the outside of both peloids and dolomite crystals, According to the EDAX data, the Al:Si-ratio is approximately 1:4, 5 and they contain Ca, K, Mg and Na. XRD data demonstrate the zeolite to be clinoptinolite.

Feldspar

Authigenic alkali feldspar is found as euhedral overgrowth on detrital rounded alkalifeldspar Fig. 8). In contrast to the detrital feldspar, it consists of almost pure $KAlSi_2O_8$, with very little substitution of Na.The SEM-SE study of sample E19 reveals small (few microns) adularia crystals with a distinctive glass-shaped crystal (Nesse, 2004), with a slightly different composition.

General thin sections descriptions

The 8 thin sections is divided into 3 groups

Group A: E04DP	Mud-supported
Group B: E13PM, E17	Clast-supported, with diagenetic zeolite
Group C: PNB, E10PM, E12PN, E16, E19	Clast-supported, cemented

Table.2 indicating composition and texture for each thin sections.

Group A: Have a relatively small content of peloids and a high content of dolomite cement and is locally matrix-supported with a heterogeneous distribution of peloids. Some parts are cement dominanted, while other parts have a subequal distribution of matrix and peloids. Peloids clearly shows two size regimes with few large peloids, and dominace of small, darkcoloured grains. There are several cavities after dissolved grains. In cemented parts, deformed grains show evidences of pressure solution. Chert and calcite cement occur.

Group B: These thin sections have a high content of detrital grains, mainly peloids. They have high porosity. Thin sections show grain-support between detrital grains. Samples are very well-sorted with medium to high-spherical grains with diameters of 0.2-0.5 mm. Elongate grains tend to have parallel orientation. The longest grain contacts are parallel to the lineation. There are both point- and concave-convex contacts between grains and several peloids and bioclasts were cracked. Small zeolite crystals may be abundant.

Group C: The Grain size varies between 0.1-2.0 mm in diameter. The texture varies between poorly sorted with two particle size regimes, 0.1 and 1.0-2.0 mm, and well sorted to very well-sorted. Grains are generally rounded to well-rounded and grain shape shows medium to high sphericity.

Discussion

Based on the petrographic study of the Djebel Onk phosphorite we have distinguished 5 steps to characterize the formation and diagenesis of the deposits.

1. Formation of peloids and sedimentation

The high amount of phosphate, presence of glauconite and abundant dissolved diatoms/radiolarian are characteristic for low low supply of terrigeneous material and suggest deposition in a condenced section (Blatt, 1982). The well-sorted grain-supported samples indicate a high kinetic energy shelf environment. All this is consistent with Djebel Onks location on the outer part of the shelf at the deposition time. The phosphatic rocks must therefore were probably deposited in an upwelling environment in the outer part of the shelf.

2. Compaction, dolomite cementation, micritisation and internal solution of dolomite crystals

Dolomite crystals which are growing on the surfaces of all detrital grains are the first cement that formed (fig.9). During the successive compaction, they have partly been pressed into softer detrital grains like peloids. This indicates that dolomite formation was early and took place while compaction was still going on. As a result of early dolomite cementation strongly cemented samples are only slightly compacted. Because of the variable composition of dolomite, the composition of the pore fluid must have changed repeatedly during precipitation. The variable composition is also recognized by the differential dissolution of dolomite zones. Although the composition of dissolved zones cannot be established, the differential dissolution must evidently be explained as a higher solubility of these zones caused by different chemistry. Many skeletal dolomite crystals are quite fragile. They are generally not broken during compaction, and dissolution must have taken place after the major compaction. The interior part of some of them is also filled by calcite cement; the partial dissolution of dolomite preceded calcite cementation. Dolomite can be formed in environments with high evaporation or with a mixture of marine and meteoric water (Tucker, 2001; Blatt 1982). There is no indication that the investigated rocks from Djebel Onk initially have been calcite cemented. Rifai (2007) suggested that the Cretaceous Egyptian phosphorites were dolomite cemented due to a mixture of meteoric and marine water caused by a transgression. This mechanism can not be transferred to the phosphate rocks of Djebel Onk deposits where the deposition in Thanetian is not followed by transgression and regression (Guiraud et al., 2005). A regression might also have led to mixing of marine and meteoric water, which may have been a cemented device. However, this process does not explain the formation of the overlying ca. 50 m Ypressian dolomite (Rifai, 2007). The evaporate environment during the formation of the Lutesian gypsum may have caused a flow of hypersaline brine through the underlying sediment and thus caused dolomite to precipitate (Blatt, 1982). The variation in Mg- content of the dolomite may reflect variable composition of the brine. On the other hand, early precipitation of dolomite cement is also promoted by anoxic diagenetic environments with significant sulphate reduction (Blatt, 1982).

3. Calcite cementation

Calcite cementation is a minor cement although it may locally dominate. It encloses dolomite and is also found in intracrystalline porosity in partly dissolved zoned dolomite crystals. This indicates that calcite formed after precipitation and the successive partial dissolution of dolomite. Calcite is also found inside compactional fractures in detrital peloids, and in thin veins crosscutting in the sample.

4. Dissolution of biogenic silica, crystallisation of chert, alkali feldspar and clinoptinolite

Chert, alkali feldspar and zeolite minerals are common diagenetic minerals (Tucker, 2001). The precipitation of chert and zeolite requires a high supply rate of dissolved silica, which may be caused by dissolution of volcaninc rock fragment or biogenic silica (Weibel et al. in press). Biogenic silica tends to shift the equilibrium towards microcrystalline quartz/chert, whereas volcanic fragments also supply Al^{3+} for zeolites. However, environments with abundant biogenic silica commonly produce chert and zeolite (Karpoff et el., 2007; Weibel et., in press). A high K^+ activity in pore fluids may promote the precipitation of potassium rich zeolites as clinoptilolite, but also the precipitation of K-feldspar. Most authigenic K-feldspar is precipitated as overgrowth on detrital feldspar grains, but it is also found as micron-sized euhedral grains which were probably nucleated on the surface of phosphate peloids.

5. Regression, uplift and erosion

After deposition of the Thanetian sediments, the coastline slowly moved further north. Shortly after the Lutetian a regional regression took place in relation to an epeirogenic phase, presumably associated with the Atlas orogeny. Uplift and erosion resulted in the present exposure of Thantian phospohorites in Djebel Onk, while the succession was partly covered by Miocene to Holocene clastic deposits. This phase may have occurred simultaneously with steps 3 and 4. Samples show signs of compaction, but the overburden has been quite small, and compaction has mainly been mediated by deformation and solution of phosphatic grains. The lithological succession (Fig. 12) indicates a burial depth of at least 200 m before uplift and erosion shortly after the Lutetian. Miocene and younger deposits have a variable distribution and are thin across the Djebel Onk.

Conclusion

Phosphatic rocks of Djebel Onk, Algeria were described. From the petrographic and qualitative chemical analyses seven of eight samples are classified as phosclast-grainstone phosphate rocks, while a single sample is classified as a phosclast-grainstone phosphatic rock. Apatite peloides, bioclasts and ooids dominate. Cement is mainly dolomite with minor quantities of calcite, chert, K-feldspar, and clinoptinolite. These observations are in accordance with previous studies. Five steps are suggested for the evolution of the phosphorite: 1) Formation and deposition of apatite peloids, bioclasts and ooids on the outer part of the shelf. 2) Dolomite cementation and compaction. 3) Calcite cementation. 4) Dissolution of biogenic silica and the formation of chert, alkalifeldspar and clinoptinolite. 5) Uplift and erosion.

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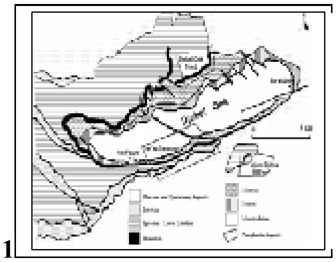
Table.1. Mineral identification in XRD

Test	Main component	bicomponent
E10PM	Apatite,Dolomite	Clinoptionolite,Calcite
E12PN	Apatite,Dolomite	Clinoptionolite,Alkali,feldspare,Quartz
E13PM	Apatite	Clinoptionolite
E16	Apatite,Dolomite	

Table 2. Texteral data from polarisation microscope

Sample number	Grain size	Sorting degree	Roundness	Sphersity(grein form)	Matrix(M)-or clast(K) supported	Punkt(P) or concave –convex (K)contact	Imbrication
E04DP	0.10-0.25 and0.2.0	Poorly sorted - in 2 size regimes	Small clasts:well rounded Large clasts:Subangular	Small clasts:high Large clasts:low	M	No actual contact but	_
E10PM	0.25-1.0	wellsorted		Medium	K	More	_
E13PM	0.2-0.5	Very wellsorted	Rounded-well rounded	High	K	P and K	Yes
E17	0.2	Very wellsorted	rounded	Medium-high	K	P dominant	Yes
E16	0.1 and 0.5	wellsorted	Well rounded	Medium-high	K	P dominant	_
E12PN	0.1 and 0.5	Moderatesorted	rounded	high	K	P and K	_
PNB	0.25-0.5	wellsorted	Well rounded	Medium	K	P and K	_
E19	0.1 and 1.0-0.2	Poorly sorted-2 size regimes	rounded	Medium	K	P	_

1 

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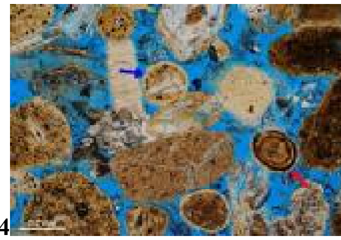
4 

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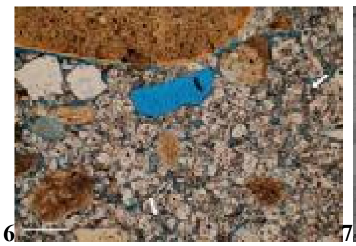
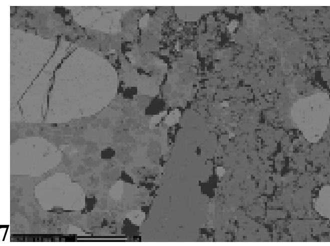
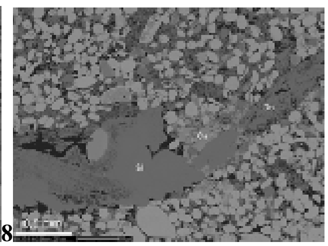
6 

7 

8 

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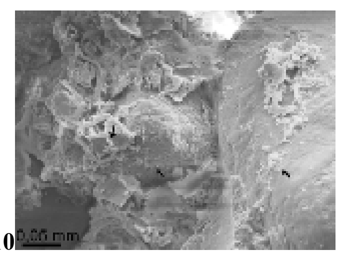
10 

Fig.1: Geological sketch map of the phosphate ore deposit (Djebel Onk) Lithostratigraphy: The site Djebel Onk lies in the north-east Algeria. and the location of the two sites Kef es Sennoun and Djemi Djema in the vicinity of Djebel Onk. Fig. 2: The top and the bottom part of Kef es Sennoun . Fig.3: General and zone out peloides. Fig.4: Red arrow: Ooid. Blue arrow: Peloid with a bone fragment as core. Fig.5: Solution Structure .Fig.8, pore-spaces filled with dolomite (Do), calcite (Ca) and silica (Si). Fig.6: Dolomite cement. Hypidiotop texture. The arrows mark the dusty zones with smaller crystals. Fig.7: Calcite cemented area in the left part of the picture.Fig.8. porespaces filled with dolomite (Do), calcite (Ca) and silica (Si). Fig.9: opaline silica. Fig.10: Zeolite crystals lies outside both peloids and dolomite crystals.