# SEDIMENTARY PETROGRAPHY AND ORIGIN OF PHOSPHATE PELOIDS OF THE MAZIDAĞ-DERİK AREA (MARDİN, SOUTHEAST TURKEY)

## Baki VAROL\*

ABSTRACT.— The Mazıdağ phosphate beds of the Upper Cretaceous carbonate sequence were deposited in an area of upwelling water which supplied phosphorous was deposited on the sea bottom as biogenic detritus of zoo— and phytoplankton, fish bones and scales. The biogenic accumulation with high content of organic matter and phosphorous was a prime source of the phosphate which formed the phosphate deposits of the Mazıdağ—Derik area. Commonly, currents transported the phosphatic sediments laterally, forming parallel and low angle cross laminations. In some cases, the sea floor was uplifted after upwelling periods. Consequently, some phosphate beds underwent karstification, giving rise to phoscretes and silcretes. Ground water percoalating into the karstic realm caused phosphate replacement of many carbonate grains of the shallow water limestone facies. These complex events resulted in the formation of three basic phosphate peloid types in the Mazıdağ–Derik phosphate sequence, which are classified to the following origin of peloids : (1) in situ precipitation; (2) abrasion of phosphatized intraclast and bioclast and (3) phosphate micritization of fish bones. The phosphate peloids show the following different microstructures under the electron microscopy : (1) amorphous; (2) microglobular; (3) semi-crystallized; (4) microcrystallized and (5) cementing.

### INTRODUCTION

The phosphate assemblages of the southeast Turkey (Fig. 1) occurred in the Upper Cretaceous carbonate sequence, which have the different depositional and textural characteristics. Previous studies have described the geochemistry, general petrology, and genesis of the Mazıdağ—Derik phosphate beds and reached general agreement about the origin of the phosphates related to upwelling waters (Sheldon, 1964, Köksoy, 1977; Lucas et al., 1979). In fact, upwelling is the most reasonable mechanism for the



Fig. 1 - Location map of the Mardin (Mazidağ-Derik) phosphate deposits (taken from Köksoy, 1977).

triggering of the phosphate precipitation, because cold deep sea waters can carry much dissolved phosphate and rich nutrients to the shelf zone (Kazakov, 1939; Baturin, 1982). Therefore, this hydrological regime has been applied to the formation of many ancient and modern sedimentary phosphate occurrenceses of the world (Arthur and Jenkyns, 1981; Baturin, 1982; Slansky, 1986). The model has been discussed in detail in the literature, and therefore is most treated further in this paper.

In this study, detailed sedimentary petrographic and electron microscopy examination of the phosphate rocks are presented and the genesis of the different types of the phosphate peloids within the beds is discussed. The samples bearing the phosphate peloids were collected from three sections (the Taşıt, Kasrık and Şemikan sections) in the Mazıdağ—Derik area, southwest Turkey (Fig.2).

The Upper Cretaceous sequence is basically diveded into three major lithological groups, carbonate, siliceous and phosphate rocks. The carbonates mainly consist of foraminiferal—algal mudstones, wackestones and dolostones. In some beds, biogenie packstone are present, occurring as brachiopod shell "lumachelle limestone" and whole rudist bivalves patch reef. The lithological associations indicate deep —water to shallow— water to supratidal carbonate environments.

The phosphate peloids were laid down in the limestone facies which show different depositional condition, both shallow and deep water. Likewise, the type of the peloids and associated grains reflect these major differences in depositional environment. For

Chronos tratigraph	Phosphate Lavers	Sample no.	Thickness (m.)	SYMBOL	EXPLANATIONS
Coniacian-Santonian	Sami- kan	1i - 7	10		Shale, chert, limestone
			2		Lumachelle limestone
			2		Chert breccia
		1,3	4		Limy and shaly phosphate
		10-19	3		Massive chert
			3	अंग्रें सि	Shale, chert, biogenic limestone
			2	^ <u>^</u> ^ ^ ^ ^ ^	Massive chert
	Kasrik	9 2,4	~		Limy phosphate
			-		Pelagic limestone
Turonian	Tasit	15-21-	30.70		Massive limestone with rudist
			10 15		Dolostone with chert nodules
			51-15		Lumachelle limestone
		14 12 11, 9	12		Shaly and limy phosphate
			5	2 2 2 2 2 2	Shaly limestone
		5-8	20-50		Dolostone , dolomitic limestone

Fig. 2 - Generalized columnar section of the Mazıdağ-Derik phosphate layers.

instance, pseudoolitic phosphate grains, which were assosiated with the phosphate peloids in the some beds, were only restricted to deep—water limestones which exhibit parallel and cross laminations, whereas uniform phosphate peloids with regular internal structure are only found in the shallow water carbonates, along with the phosphatized biogenic grains. Fish bones, teeth, spines, and phosphatized intraclasts are commonly in every phosphate beds, showing different environmental habitats.

Francolite (carbonate-fluorapatite) is the predominant phosphate minerals in the examined peloid samples. Additionally, some intraclasts derived from nonpelloidal phoscrete layers contain collophane, and also the peloids including bone remnants are rich in dahlite.

The phosphate peloids are the dominant component of the phosphate—bearing layers, and they are discussed in detail below.

# PHOSPHATE PELOIDS

In this study, all spherical and oval phosphate grains ranging from 0.15 to 0.50 mm in diameter are considered to be phosphate peloids (McKee and Gut-schick, 1969) regardless of their origin and internal structures. Grains larger than 0.50 mm in size are termed phosphate ovoids if rounded, and phosphate intraclasts if angular.

The phosphate peloids usually appear isotropic under the polarizing light microscope, because they are composed of very fine crystals, showing the usual character of marine phosphates (Baturin, 1982). Some peloids also may exhibit a weak anisotropy. The microinternal structures of the different types of the phosphate peloids were examined by scanning electron microscopy (SEM), under 1000–3000 magnification. Additionally, phosphate grains were scanned with an EDAX system in order to reveal the phosphate distribution.

The combination of the normal and electron microscopy examinations has led to defination of the following types of phosphate peloids. In situ precipiated peloids (zonal and nucleate or pseudoofitic)

This type of peloids refers to in situ phosphates precipitated from phosphate—rich solutions. They are diveded into two types, zonal and nucleate peloids, based on texture. The zonal peloids are between 0.15—0.20 mm in size, and have central parts which are blurry and dark colored (mostly brown). They include numerous non—phosphatized inclusions, such as iron oxide pigments, organic matter and carbonate mud. In rare case, the dark colored material covers the entire surface of the peloids. Marginal part of the peloids are transparent and more clear, and are mostly yellowish in color because dark inclusions are absent.

Nucleate peloids have a nuclei in the centers and transparent rims. Skeletal calcitic grains, minute fish bones and teeth formed peloid nuclei, and the peloids themselves served centers for the growth of the transparent phosphate rims. The internal structure is roughly similar to the concentric laminae of ooid grains; however, true concentric accretion laminae are absent and is interpreted as a phosphate pseudoolite.

The zonal and pseudoolitic assosiations are mostly found in a pelagic mud matrix showing parallel and cross laminations, and well—rounded phosphate intraclasts. The intraclasts were derived from the phosphatized mud, and suggest that bottom erosion succeeded the phosphate formation, induced by currents. The current activity concurrently caused the mixing of the different type of the phosphate grains in the same level, which lead to deposition of biopelphosphoarenite (Slansky, 1986) in the Derik-Mazıdağ phosphate beds. The rock type (Plate I, fig.l) is typical in the whole sequence of Kasrık phosphate and below levels of the Şemikan phosphate.

The zonal phosphate peloids present an inhomogeneous phosphate distribution, as seen well with EDAX scanning (Plate I, fig. 3,4). The EDAX scanning revealed that the dark and turbid central portions of the peloids have less phosphate than clear peripheral zone, and high organic matter and iron content. In the electron microscope, organic mud can be easily distinguished as its surface was covered by microswelling, fistules, and nodules, whereas the clear and transparant peripheral zone consisted of well—pocked micronodules without organic mud. According to the electron microscope data, the formation of the zonal peloid took place in two main stages, as follows.

In the initial stage, the phosphatization began as microcenters or swelling, which made up an uneven and bumpy surface on the organic mud matrix (Plate I. fig. 5). In the second stage, the bumpy surfaces were completely turned into micronodules (Plate I, fig. 6,7). The different degree of the phosphatization stages affected the colored character of the zonal peloids. For instance, where the volume of the organic mud was very high, the peloid is blurry and dark. To the contrary, the high content of phosphate gives rise to the transparent character of the peloid which is devoid of organic mud. In addition, non-nodular and/or amorphous and semi-crystallized (fusiform) phosphates have been observed in the electron microscope. The amorphous type is a homogenous mass which shows no sign of granulation and crystallization. However, in rare case, some ultra-micronodulations are present on homogenous phosphate masses (Plate I, fig.8). The semi-crystallized type mostly shows rosettes with satellite appearance (Plate II, fig.2). The fusiform habit has been attributed to an intermediate stage of crystallization between amorphous and semi-crystallized (Baturin, 1982). In the examined samples, these types were mostly found on the transparent surfaces of the peloids.

Pseudoolitic phosphate grains include both semicrystallized and micronodular varieties. The micronodules are commonly scattered as free grains on the semijcrystallized phosphate background (Plate II, fig-1)-This microtexture suggests that some mobile phosphate solutions were developed during the formation of the pseudoolitic phosphate grains. The mobile phosphate solutions may have evolved at the Sediment/sea water interface. The abundance of the pseudoolitic grains in the laminated (cross and parallel) biopelphosphoarenite indicate the depositional environment was influenced by current activity, and led to physical mobilization of the phosphate gel around some nuclei of the pseudoolites.

Peloids derived from intraclasts (non-internal structure)

These are formed as a result of physical abrasion of the undurated or semiplastic phosphate intraclasts. The rounded grains can be easily differentiated from in situ precipiated peloids by lack of internal structure. Generally, they are yellow or brown in color. Grainsize is always coarser than the other type of the phosphate peloids, ranging from 0.20 mm to 0.60 mm. Oval shapes are predominant and very diagnostic for the interpretation of this type. Similar forms have been described as egg shaped-phosphate grains "ovules" by the study of Cook (1972). In the Mazıdağ-Derik phosphate sequences, is type of peloid was largely accumulated in the biopelphosphoarenites which were deposited by currents. Consequently, they were more rounded than the ones in the shallow-water carbonate facies. On the other hand, the phosphate peloids derived from intraclasts show different color properties, probably depending on the environmental conditions. The types with light colors (generally yellow) are found within the deep-water limestone, and have a high phosphate content. Shallow water types are darker (brownish) and less phosphatized. The latter types are commonly associated with phosphate intraclasts derived from phoscrete layers. Their internal structures are very similar to each other, which imply genetic relationship between the phosphate intraclasts and peloids in some shallow water limestones.

In the electron microscope examinations, the microinternal structures of this group are characterized by an organic mud which was subjected to different degrees of phosphate replacement. The samples belonging to deep sea facies were made up of diatom mud. Generally, the microholes of the diatom tests can be discernible within the phosphatized mud. In some cases, the microholes were filled with a cement of microapatite crystals (Plate II, fig.3). Samples taken from shallow water limestone do not contain any trace of diatom valves, and they are mostly recognized by microcrystallized (tabular or elongated) apatites, replacing the micrite matrix (Plate II, fig. 4).

## Peloids derived from bioclasts

This type of the phosphate peloids usually makes up non—economic phosphate beds and consequently it has not been previously studied in detail. The content of phosphate is low. However, they exhibit some interesting diagenetic properties, which help to define the phosphatization conditions and processes within the shallow water limestones.

The peloids are often angular and coarse—grained (0.25—0.75 mm). In most cases, traces of shell structures are retained within the peloids. The original shell structures can be easily observed by light microscope examination with high magnifications in case of low-grade phosphatization. This suggests that disaggregated shell fragments in the intertidal—subtidal limestones underwent phosphate replacement. Commonly brachiopod shells and outer walls of gastropods were favored the phosphate replacement.

Neomorphic sparite (pseudosparite) is always associated with this kind of phosphate peloids. The association implies diagenetic effects in the fresh water phreatic zone during phospatization (Longman, 1980). Phosphatization through ground water, which is rich in dissolved phosphate, has been noted by Shalkowitz (1972). The worker considered that phosphate bearing ground water must be a prime agency for the phosphate replacement of the biogenic grains in the shallowwater limestone facies.

Peloids formed by phospho—micritization of fish bones (with regular internal structure)

This type of the phosphate peloids may be pre-

sent within some level of the Mazıdağ-Derik phosphates, but they have been commonly developed as the massive phosphate deposits in the Semikan phosphate layers. They are dark in color, and show a gradualy lightening towards the exterior parts of the peloid grains (Plate I, fig.2). Their shape, petrographic character, and host rock texture are entirely different from other types. Grain-size distribution of the peloids is uniform (averaging 0.15 mm) and sorting is very good. The rock is composed mostly of pure phosphate peloids, and the other usual constituents such as pseudoolite, bioclast, ihtraclast and various carbonate grains are either diminished or completely absent in these layers. Compaction is very weak, and also the ratio of cementing is very low. Overall, phosphate peloids are bounded by either grain contact or a thin calcite cement. Porosity is very high, up to 20-30 percent, and consequently the rock is friable, and disaggregated into sandy. In the light microscope, the peloids are distinguished by a regular internal structure, mostly including a micritic central zone and a light yellow a peripheral zone which shows weak anisotropy and some remnants of the fish bones.

In the electron microscope, the phosphate peloids exhibit microrelief within the phosphatized mass. These structures are very similar to elongated microchannels of the fish bones (Marshall and Cook, 1980). The probable channels were covered with microphosphate granules or apatite crystals grown perpendicularly on the wall of the channel (Plate II, fig.6,7,8). This structural character implies that fish bones were phosphatized, creating the phosphate peloids. Similar textures have been observed by Cook (1980), and the processes have been attributed to phosphomicritization of the fish bones, induced by microalgae. Indeed, in the examined samples, in addition to the channel-like microstructures, the micritic appereance and weak anisotropy resulting from partial phosphatization of the fish bones supports the hypothesis that the fish bones were converted to the phosphate peloids. Seyhan et al. (1973) also reported phosphate grains with bonebrecciated texture in the Semikan phosphate layers.

## GENESISOFPELOIDS

In the Mazıdağ-Derik phosphate beds, in situ zonal peloids always occur in organic mud which is rich in zoo-phytoplankton and fish remnants. This indicates that there is a causal relationship between in situ peloids and the organic mud. Indeed, many ancient and phosphate beds were laid down in diatom mud, and phosphate peloids were diagenetically formed within the organic mud, instead of by direct precipitation from sea water (Baturin, 1971; Baturin and Bezrukov, 1979; Balson, 1980). A few samples are interpreted as having directly precipiated from sea water as oolithic phosphate beds (Arthur and Jenkyns, 1981). According to Brice and Calvert (1978), in the actively upwelling zones of the continental margin of southwest Africa, Peru, and Chile interstital waters include dissolved phosphate much more than ten times the concentration in the surrounding sea water. Likewise, Baturin (1982) reported that the initial phosphate formation began within organic mud when the phosphate concentration reached 5 to 9 mgl<sup>-1</sup> in the interstital water. At this stage, all of the non-phosphatized remnants, such as very minute fish bones, diatom tests and other carbonate particles were precipitated, along with phosphate. The mixing material gave rise to form a dirty, dark and blurry central zone of the phosphate peloids. At the later stage, pure phosphate solutions cleaned from non-phosphatized remnants led to precipitation of the transparent exterior part of the peloids. The different stages and the different solutions during the formation of phosphate peloids should be effective to evolve the in situ zonal peloid of the Mazıdağ-Derik phosphate beds. Indeed, examined samples of this type of peloids generally contain an inner zonation. The central portions contain organic mud and less phosphate (bumpy surface); this suggests that the initial phosphate growth started from these organic mud surface. Then, the granulation up to full micronodules created the clear and transparent exterior zones of the peloids; this processes was probably enhanced by current movements which led to roll of

peloids on the sea bottom. The presence of free micronodules on the pseudoolite surfaces support the conclusion that a mobile phosphate solution caused the growth of the in situ peloids. Hence, sedimentological and hydrological conditions such as current activity should be an important controlling factor for the evolution of the phosphate peloids, along with geochemical equilibrium of the interstital water. On the other hand, Bromley (1967) and Shalkowitz (1973) have reported that bacterial oxidation served as the prime agency for the release of phosphate from organic carbon, during the uplift of the sea water at the interface of the sediment and sea water.

That the sea level fluctuated greatly during deposition of the phosphate succession of the Mazıdağ-Derik is cleary indicated by the alternations of the deep -and shallow water-phosphate and carbonate facies. In this light of this data, in situ peloids have probably been formed in the following steps : (1) Deposition of an organic mud, containing abundant zooplankton and phytoplankton, during period of upwelling water; (2) Starting of the initial granulation on the surface of organic mud, in slightly reducing conditions; here, diatom tests might have served as nuclei for the triggering of the phosphate precipitation and/or initial nodulations; (3) Uplifting of the sea bottom, with current activity enhancing the growth of the in situ peloids under weak oxiding conditions, in which the phosphate is released from organic matter much faster than in reducing condition. At this latter stage, some phosphate solutions could be mobile on the sea bottom, induced by currents. The physical activity might be a prime agency for the formation of the phosphate pseudoolite material around the nucleis as well as the growth of the in situ zonal peloids.

The phosphate peloids derived from the intraclasts resulted from the rolling of both soft intraclasts and hard intraclasts. The soft material was probably turned upypartly lithified, phosphatized mud. Current activity favored the formation of these types, as cross and parallel laminations were associated with the layers which had the soft intraclasts and the relavent phosphate peloid. Hard intraclasts are mostly found in the shallow water limestone or near the karstic phosphate beds, suggesting they are derived from the phoscrete surfaces. In fact, the internal structures of these phosphate peloids are very similar to those of the phoscrete samples. On the other hand, some burrows on these grains can be attributed to biogenic erosion, which likely aided in rounding the hard phosphate fragments.

The peloids derived from bioclasts have been only observed in the shallow water limestones. This

situation suggests that a part of the phosphatization process could have occured in the coastal area. As a matter of fact, Ames (1959) experimentally calculated that even a very low phosphate concentrations (0.1 ppm  $PO_4^{-3}$ ) in solutions can achieve the replacement of a calcitic shell. Likewise, Cook (1982) has proved that the tidal—flat limestones underwent phosphatization through replacement by ground water percoalating from nearby phosphate karst. Karstic surfaces, which are common in the Mazıdağ—Derik phosphate sequence, could have been a major source



Fig. 3 — Diagrammatic model showing development of phosphate peloids from fish bones by phospho—micritization and physical abrasion. I—Bone piles; II—The pile's phospho—micritization of the bone fragments, by microbiological processes (Schizomycophyta). This phase is shown on Plate II, fig.5; III-Disappearance of bone textures with increase of the phosphate content; IV-The conversion of the disintegrated fish bones, which have undergone the physical alteration by microbiological processes, to phosphate peloids.

for phosphate, which could have replaced biogenic grains in coastal limestone that were in contact with ground water.

The last phosphate pelloid type associated with fish bone beds, can be attributed to microbiological activity. Similar examples have been interpreted as phosphatization of the fish bones via the activity of (Schizomycophyta) the microalga (Soundry and Nathan, 1980). The processes is a phospho-micritization in association with physical abrasion, leading to peloid formation. This occurs in the same way as micritization of a calcitic shell through microboring algae (Soudry, 1979; Friedman et al., 1971; Bathurst, 1976). Especially, physical abrasion with microalgal activity could be a prime agency to construct the pelloidal forms in the studied samples.

In the electron microscope, regular microgrooves and longitudinal microrelief reflect the remnants of the bone texture in the pelloidal phosphate mass. Moreover, micritic inner zones should result from a phospho-micritization process, and also minor bone fragments within the weak anisotropic phosphate peloids suggest that this phosphate peloid type was generated from fish bone material by phosphomicritization under the influence of microalgae. On the other hand, the low content of the non-phosphatized material and calcite cement indicate a closed system during phosphatization of the fish bones. The following sequence is proposed: (1) The piles of the fish bones experienced the microbiogenical attact in the coastal area. The period might have been long, with non and/ or slow sedimentation; (2) The microbiogenic activity increased with time and some portions of the fishbones were converted to the phosphate (Plate II, fig. 5); (3) The original fish bone textures were severely disturbed by the processes of phosphomicritization; (4) The phosphatized fish bones disintegrated into the pelloidal grains. The conversion from fish bones to the phosphate oeloids is illustrated diagramatically in Figure 3.

# CONCLUSIONS

The phosphate peloids in the Mazıdağ-Derik

area resulted from a chain of complex events. The first type occured under the open marine conditions and precipftated as microswellings and nodules from interstital water rich in dissolved phosphate. Sometimes, microcrystalline to semi—crystallized- types were associated with the nodular phosphate formation. The micronodules were perhaps mobile onto the sea bottom during the formation of the pseudoolitic phosphate, which suggests active currents during growth of the phosphate peloids. In this study, this type is interpreted as in situ zonal peloids.

The other types of the phosphate peloids were mostly concentrated in the shallow water carbonate facieses, and they formed through different processes than the former type. Ground water rich in dissolved phosphate and microbiogenic activity were the prime agencies for the. phosphatization and the production of the pelloid grains. Ground water, which percolated into the phosphate karst nearby the limestone realms led to phosphate replacement of biogenic grains. Microbiological activity through prosphomicritization *by Schizomycophyta* or a similar algae, aided by physical abrasion, formed phosphate peloids from fish bones as the condensed phosphate deposits.

The environment in which phosphate was formed underwent sea level fluctuions during or soon after phosphate formation, and consequently different types of phosphate peloids were often mixed each other in the same bed in the Derik-Mazıdağ phosphate succession.

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# PLATES

# PLATE-I

- Fig. 1 The zonal internal texture of light—colored, in situ formed peloid grains. The dark colored central parts show organic material and the remnants of diatomaceous mud inclusions which exhibit a range phosphatization.
  Ta-12 (Taşıt), X 30.
- Fig. 2 Homogenous, dark colored phosphate peloids, formed by phospho micritization of fish bone.
  Şe-3 (Şemikan),X 30.
- Fig. 3,4 Scanning with the EDAX, the zonal peloids show an inhomogenous phosphate distribution. Ka-9 (Kasrık).
- Fig. 5,6 Phosphate within the interior of a phosphate peloid, showing micro-swellings and micro-nodules. The dark colored botton part is diatomaceous mud. Ta-14.
- Fig. 7 Pure phosphate micronodular accumulations, the organic mud was greatly disappeared within themicronodularmass. This material represents the pure and clear rim of the peloids. Ta-12.
- Fig. 8 Amorphous phosphate, apart from very small and free micronodules, no granulation has been developed. Ka-4.













20KV X3358 184 043 12126 CRC







20KU X1499 100 045 12116 CRC



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# PLATE-II

- Fig. 1 The free micronodules in the interior of the pseudooid-type phosphate peloids. This reveals the water's chemical transport at the interface of the sediment and sea water. Ta-11.
- Fig. 2 Rosette and fusiform segregations of phosphate in a light-colored peloids. Şe-l.
- Fig. 3 The developing microapatite crystals cementing the micropores of diatom tests. Ka-2.
- Fig. 4 The cylindrical to flat microcrystalline apatite crystal aggregates which replaced the carbonate mud matrix. The internal texture of a typical peloid derived from intraclasts. Ta-4.
- Fig. 5 A fish bone fragment in early stage of conversion to a phosphate peloid by phospho-micritization. Ta-9, X 25.
- Fig. 6 An ordered bone texture, showing typical internal structure of fish bone fragment. Se-3.
- Fig. 7,8— The internal texture of a peloids formed by phospho-micritization. The micro-granules and crystals have been developed within the ordered framework of the primary texture. Microrelief on the peloid surfaces suggests relict primary bone texture.

Şe-3.







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0,3mm





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