



PHOSPHORUS CONCENTRATION MECHANISMS AND PHOSPHORITE FORMATION, CASE STUDY: THE FORMATION OF FRANCOLITE IN AKASHAT PHOSPHORITE OF EASTERN TETHYS, IRAQI WESTERN DESERT

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EXTENDED ABSTRACT

L'aumento del contenuto di P_2O_5 da 70 ppb nell'acqua di mare a oltre il 30% in peso nelle fosforiti marine è un processo a più stadi, che include: l'intrappolamento biologico di P dall'acqua di mare, l'arricchimento di P per decadimento, il flusso inverso di P all'acqua di mare, le correnti di risalita, la formazione di fasi fosfatiche, i processi diagenetici precoci e tardivi (di litificazione, meccanici, chimici e biologici) che portano alla formazione e alla discriminazione dei grani fosfatici (peloidi, coproliti, ooides, cortoidi, denti di pesce e resti ossei...ecc.). Lo stadio finale rappresenta la ridistribuzione della facies fosfatica negli ambienti deposizionali lungo la piattaforma continentale.

I processi di biogenesi e diagenesi rappresentano i due fattori principali che controllano la concentrazione di fosforo nell'acqua di mare e la formazione di fosforiti in Iraq, tra i paesi del Medio Oriente che si affacciano sulle coste meridionali del mare della Tetide. I processi biogenici concentrano il contenuto di fosforo come P_2O_5 fino a circa il 5-7% in peso, mentre i processi diagenetici aumentano il P_2O_5 a più del 18% in peso e qualche volta possono raggiungere circa il 34% in peso. Il presente studio supporta il meccanismo proposto da Baturin (1982) per l'arricchimento di P e la formazione della fosforite. A seconda delle ipotesi proposte, si può descrivere il meccanismo generale per la formazioni di fosforite biogenica-diagenetica.

Le fosforiti di Akashat sono costituite principalmente da francolite, che dipende dalla composizione chimica dell'acqua interstiziale. P, Ca e Sr sono correlati all'attività organica del decadimento dei batteri nell'acqua interstiziale. Il materiale organico contribuisce alla raccolta di alcuni elementi come V, Pb, As e HREE dall'acqua di mare e li fissa sui grani fosfatici durante la loro crescita cumulativa, mentre Na, S, U, Y e LREE riflettono le proprietà chimiche dell'acqua di mare poco profonda in corrispondenza della piattaforma continentale. Questo ambiente rappresenta l'area di formazione della francolite che è esposta a un parziale isolamento dal mare aperto da locali barre sottomarine, come evidenziato da un leggero aumento della salinità e dell'alcalinità. La concentrazione (mole/formula) del carbonato nella francolite è correlata ai processi multidiagenetici verso la fase più stabile (fluorapatite), unitamente all'associazione di anomalie positive e negative di Ce ed Eu, rispettivamente, che indicano condizioni non ossidanti e senza attività vulcanica sottomarina nella formazione di francolite. In definitiva sia la formazione primaria sia il processo diagenetico hanno effetti simili sulla chimica cristallina della francolite.

Questo studio dimostra che non esiste alcuna relazione tra il F aggiuntivo calcolato dall'analisi chimica e l'asse a , ma piuttosto una relazione lineare con un asse c che ne permette la sua stima. Il presente studio concorda con la visione della sostituzione del fosfato con il carbonato + ioni fluoruro per due motivi: primo, la sostituzione del tetraedro fosfato con lo pseudo-tetraedro di entrambi $CO_3^{2-} + F^-$, e secondo, la sostituzione di $CO_3^{2-} + F^-$, con carica totale -3, al posto del fosfato (PO_4^{3-}) soddisfa il bilancio delle cariche. La sostituzione del fosfato con il carbonato comporta una diminuzione dell'asse a e un leggero aumento dell'asse c . La lunghezza dell'asse a può essere utilizzata per la stima del contenuto di carbonato nella francolite.

Pertanto, in questa sede, si suggerisce di utilizzare le differenze nella distanza angolare delle riflessioni 310 e 002 e le riflessioni 002 e 310. Sembra, infatti, che il miglior risultato nella definizione della lunghezza dell'asse a sia correlato alla differenza nella distanza angolare delle riflessioni 002 e 310.



ABSTRACT

The increasing in P_2O_5 content from 70 ppb in seawater to more than 30 wt% in marine phosphorites is a multi-stage process, which includes: the biological trapping of P from the sea, the enrichment of P by decay, the reverse fluxing of P to seawater, the upwelling currents, the formation of phosphatic phases, the early and late diagenetic processes (lithification, mechanical, chemical and biological) which lead to the formation and discrimination of the phosphatic grains (peloids, coprolites, ooides, cortoides, and fish teeth and bone remnants...etc.). The final stage represents the redistribution of phosphatic facies in depositional environments along the continental shelf. Depending upon the suggested views, one can describe the general mechanism as the biogenic – diagenetic phosphorite formations.

Akashat phosphorites have mainly consisted of francolite, which depends on the chemical composition of interstitial water. P, Ca and Sr are related to the organic activity of the decay by bacteria in the interstitial water within the upper part of the sea floor mud. The organic material contributes in the collection of some elements like V, Pb, As and HREE from seawater and fixed them on phosphatic grains during the accumulative growth of the phosphatic grains., whereas Na, S, U, Y, and LREE reflect the chemical properties of the seawater in the shallow continental shelf. This environment represents the Francolite formation area which is exposed to partial isolation from the open sea by the local submarine bars, reflected by a slight increase in salinity and alkalinity. The mole/formula of carbonate in Francolite related to the multi diagenetic processes toward the more stable phase (fluorapatite). In addition to the association of positive and negative anomalies of Ce and Eu, respectively, which indicated non-oxidizing conditions and without sub-marine volcanic activity through francolite formation. Both roles of primary formation and the diagenetic process play similar effects on the crystal chemistry of francolite.

KEYWORDS: *phosphorites, francolite, phosphates, Akashat Fm., phosphatic concentration, apatite*

INTRODUCTION

The phosphorite rock formation events in the phosphorus-bearing formations in Iraq are belong to the phosphate deposits of the ancient Tethyan Sea (AL-BASSAM, 1992). Tethyan phosphorites span over a wide range of time (~90 my) where deposition commenced on Cretaceous and continue through to Eocene (SOUDRY *et alii*, 2004). The Tethyan phosphorites are commonly known as Arabian-African Phosphorites Giant Belt (AAPGB) which extends to as far as Colombia to the west, through Venezuela, Brazil, and North Africa, to the middle east, Iran, India, China, and Australia at the far east (NOTHOLT, 1980; SHALTAMI *et alii*, 2018). Accordingly, the (AAPGB) is

divided into various isolated basins in Africa continent. Congo-Niger, Senegal, Western Sahara, Morocco, Algeria, Tunisia and Egypt, and in Asia continent: East Mediterranean countries (EMC), central Asia (Russia), India, China, and Australia. The phosphorites of (EMC) exposed at different stratigraphic levels (Turanian - Eocene) and in different locations of Turkey, Syria, Jordan, Palestine, Saudi Arabia, and Iraq, (AL-SHEREIDEH *et alii*, 2010) (Fig. 1).

The (AAPGB) contains the largest accumulation of sedimentary phosphorites, which amount to 130×10^9 metric tons (~66% of world reserve) (PUFAHL *et alii*, 2003). The calculation of reserve shows a fabulous quantity of P_2O_5 (26×10^9 metric tons) which justified detailed investigation and look in-depth at the various aspects of (AAPGB) including main factors determining phosphorites formation as climatic, biological, oceanographic processes and tectonic. Perhaps, the best way to study the formation factors is to take an example of phosphorites of discrete age and finding possible application of a solution to common problems with other world phosphorites (as hopefully intended in the present study).

The discovery of phosphorites in Iraq is a result radiometric survey of the western region extended from Rutba city to the International Iraqi/Jordan border (SMITH, 1954). Cobbett (1954) assured this finding and thought that eight phosphorites' horizons are the source of the radiation. Buday and Hak (1980) conclude that Iraqi phosphorites extended in age, from Campanian to middle Eocene, with the highest reserve of Paleocene phosphorites exposed at Akashat area (Fig. 1). The last remark is the reason for the selection of Akashat phosphorites in the present study.

Francolite is one of the stable calcium phosphate phases with composition between end-member minerals of apatite series. The chemical formula of Francolite is $[Ca_{10}(PO_4)_6CO_3F_2]$ which also called carbonate-fluorapatite or sometimes named marine apatite (MCARTHUR, 1985). Apatite mineral belongs to the hexagonal system, class (6/m), space group (P63/m) and commonly occurs in a crystal of long prismatic habit, some short prismatic or tabular. Usually, terminated by a prominent pyramid of the first order or frequently a basal plane. Some crystal show faces of hexagonal dipyrmaid which reveals the true symmetry Also occurs in massive granular to compact massive. It appears from the crystal composition of apatite that calcium occupies two sites. Calcium in the first site Ca(I) is in 9-coordination where Ca in the site Ca(II) is with 7-coordination. Such calcium distribution leads to a wide range of elements (predominantly divalent elements) that replace the calcium in both sites (I) & (II) (LANFRANCO *et alii*, 2004).

Elements replacement in Ca(I) site are associated with no change in crystal parameter (a & c) because the location of this site is on tri-axial and replacement effect is homogeneous. On the other hand, little change in crystal parameter is noticed in case

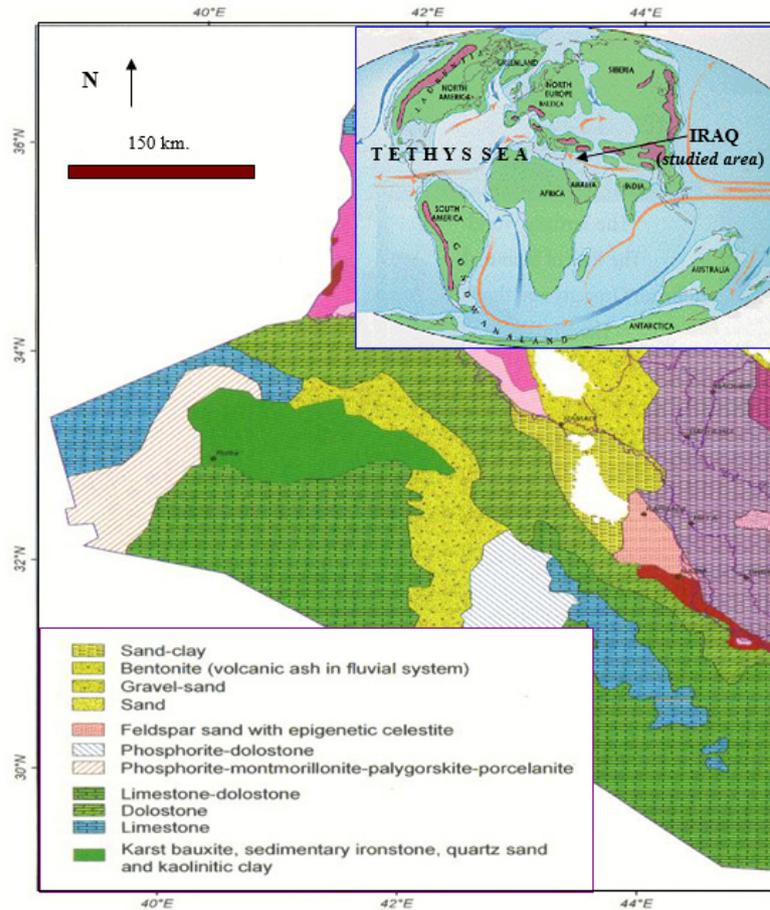


Fig. 1 - Location on ancient Tethys sea and the geological map of rocks in Iraqi western desert. (after BUDAY & JASSIM, 1984)

element replacement of calcium in the site (II), due to the effect of diagenesis, whereas elements replaced in Ca(I) were derived from the primary deposition environment of Francolite. Crystal structure of apatite displayed in Fig. 2 which shows both sites of calcium concerning the mid-channel of the crystal network.

The mechanism of increasing Phosphorous content in seawater has attracted great attention among researchers and this led to huge numbers of published and unpublished studies that suggest different mechanisms for the increase in phosphorous content. However, many studies stressed the role of organic materials and interstitial water of the ocean floor mud, in the formation of marine apatite.

The present study is intended to share the discussion on the genesis and mechanism of increasing phosphorous content and the formation of phosphorites.

GEOLOGY OF AKASHAT PHOSPHORITES

Most Iraqi phosphorites (including Akashat phosphorites) are exposed within the Rutba-Jazira zone in the eastern part of

the Arabian platform located to the west of Iraq (Fig. 1). The separation of Rutba and Jazira belts from the Rutba-Jazira zone is the result of east-west subsidence of the sedimentary Anah basin during the upper cretaceous time and leading to Rutba uplift. The Rutba uplift comprised sediment beds of Paleozoic to recent (including facies of Iraqi phosphorites) with bed slope not more than 1° in most cases. It is thought that the vertical movement of rocks of basement mass (part of the huge regional structure) reflected on the sedimentary cover leading to Rutba uplift (BUDAY & JASSIM, 1984).

The phosphorites-bearing Paleocene succession in Akashat mine is located to the northwest of Ga'ara depression at Iraqi western desert. Akashat Formation consists of three members: (i) Trefawi member (Lower Paleocene) which represents the oldest unit and belongs to the Danian age. The rocks comprised of a periodical succession of sandstones, shales, marls, porcelanites, and limestones. The rocks are enriched with Planktonic and Benthonic foraminifera. The phosphorites are distinguished by thin beds peloidal and foraminiferal ooidal phosphorites with

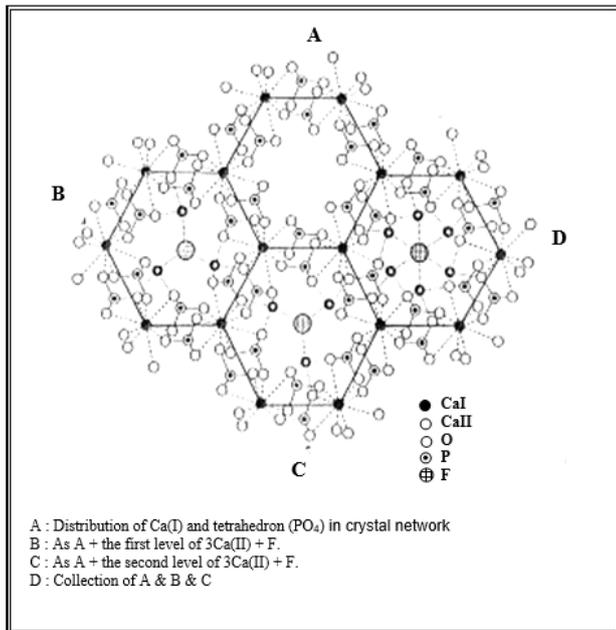


Fig. 2 - Crystal structure and distribution of Ions in crystal network of apatite (ALTSCHULER *et alii*, 1958)

cementing material of phosphatic micrite and micrite, which all reflect the shoal opens inner platform (MUHAMED, 1993). (ii) Herri member (Middle Paleocene) which is the most important economic unit, as it includes phosphorites currently exploited for phosphatic fertilizers production in The General Company of Phosphates in Al-Qaim area in Iraq. Herri member is widely distributed in the Iraqi western desert and it is distinguished by the variable thickness and reaches 10m. at Halkom wadi and up to 45 m. at Trefawi wadi (AL-BASSAM *et alii*, 1990). The Herri member divided into three main parts: below phosphorites; phosphorites and overburden rocks. Detail discussion is followed later on. (iii) Dwaima member (Upper Paleocene) distributed widely in the Western Desert with a variable thickness which may reach 20 m. at outcrops, in north-east Akashat area and extended to the international Iraq/Saudi border. The unit consists of cycles of three types of rocks: phosphorites (bones, intraclasts, and unsorted oolites), limestone (chert nodules) and clay beds. (AL-BASSAM *et alii*, 1990).

THE HERRI MEMBER ROCKS

The Herri member rocks consist of phosphorite layers that represent the industrial rocks, it overlay a one-meter thickness of thinly bedded of gray and hard bone oolitic phosphatic limestone which is enriched with pelecypods and Gastropoda (Fig. 3), and distinguished by high phosphate content ($P_2O_5 = 22$ wt%). Upward in the succession, three phosphorites bed alternate with a similar thickness of three limestone beds (40 cm each) making total thickness about 2.5 m. The gray to grayish colored

phosphorites beds are of an intermediate hardness and its P_2O_5 content may reach 17 wt%. In contrast, the limestone beds show higher hardness and appear white.

The succeeded rocks include several peloidal phosphorite beds of variable thickness (7 m total) and distinguished by a range of colors (white, dark gray and dark yellowish-brown), by variable hardness (friable and well sorted to very tough) and by a high content of fish's bone and teeth remains. The cementing material consists of micrite and phosphatic micrite with the iron oxides (limonite). The P_2O_5 content may reach 25 wt%.

The overburden bed is distinguished by rugged topography and can be divided into two parts: the lower part of 4 m. thickness consists of white to pale gray, very hard and well-crystallized limestone enriched with fossils dominated by pelecypods. Upward in the succession, two thin (30 cm) beds of variable colors (pink, yellow, violet, reddish-brown), intermediate hardness to hard calcareous claystone. The upper part of 7.0-10.5 m. thickness consists of white, thick and very hard limestone and chalky limestone (with the occasional presence of pelecypods and Gastropods) alternate with four horizons (10 cm thickness) of chert nodule zones, covered by very thin laminae of iron oxides. The upper lithological units consist of thin beds (15 cm) of dark brown fissile and laminated cross-bedding claystone.

PHOSPHOROUS AVAILABILITY AND DEPLETION IN SEAWATER

Seawater phosphorous content is (70-75) $\mu\text{g/liter}$ (SLANSKY, 1986), which present in various forms: dissolved inorganic species like HPO_4^{2-} which make (85-90)% of the dissolved inorganic phosphorous (BENTOR, 1980; LEVLIN, 2003), dissolved organic ions and in the suspended form adsorbed and/or within suspended organic materials (Baturin, 1982). Sea water phosphorous is derived from different sources, for example, rives water share of $(1.5-1.75) \times 10^6$ ton/year in the form of dissolved phosphorous, and about 0.06×10^6 ton/year is derived from submarine volcanic activity (BATURIN, 1982; BENTOR, 1980). The share (2%) of oxidation of organic materials is low in the balance of seawater dissolved phosphorous (BENTOR, 1980). The suspended form of seawater phosphorous is derived from the atmosphere fallout (including storms) which amount to $(1.1-1.4) \times 10^6$ ton/year (BATURIN, 1982).

Various geochemical and biochemical processes may lead to a loss in seawater phosphorous. Adsorption on iron oxides and hydroxides (GAO & MUCCI, 2003) and with iron-manganese nodules (BERNER, 1973) in (BATURIN, 1982). Adsorption on clay minerals is a plausible geochemical mechanism of phosphorous loss. Biogeochemical processes may lead to loss of seawater phosphorous and include: bacteria associated with organic materials, which may extract the great amount of phosphorous with fixation rate may reach up to 30 $\mu\text{g/l/day}$ (SOROKIN &

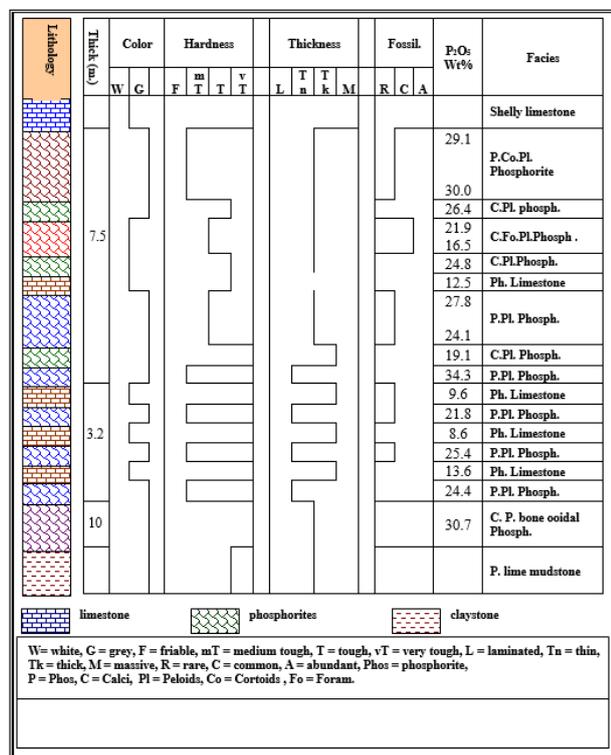


Fig. 3 - The geological section of industrial rocks of Akashat phosphorite in Akashat mine

VYSHKVARTSER, 1974) in (BATURIN, 1982). Phytoplankton plays a role in phosphorous trapping from seawater and fixation within living materials (ELBAZ-POULICHET *et alii*, 2000).

The input and output of seawater phosphorous lead to the state of seawater undersaturation concerning calcium phosphate and deprived direct precipitation of apatite from seawater (BENTOR, 1980). As a result of the last conclusion, different studies appeared through the last tens of years, dealing with the mechanism of up-grade of phosphorous content (70-75) µg/l in seawater to about 30% P₂O₅ in phosphorites. The following is a brief revision of the previous studies.

PREVIOUS STUDIES

Most of the previous studies were concerned with finding one single primary mechanism of phosphorites formation represented by the study of KAZAKOV (1937) in (BENTOR, 1980) which is based on the believe of the existence of a relation between phosphorites precipitation and marine upwelling currents. This believe is backed by the environmental change to conditions more suitable for phosphosites precipitation as the upward movement of cold currents seeking warm regions accompanied by loss of CO₂, which led to an increase in pH values. Present phosphorites of 50-200 m depth, were well explained by KAZAKOV's theory. Later, KAZAKOV's views were

criticized based on the absence of Ca/Mg suitable value of 5.2 necessaries for phosphorites formation in seawater. This led to SAREUKO (1980) in (SLANSKY, 1986) to conclude that apatite phases not directly precipitated in open seawater environment, moreover, calcite of 0.06 wt% P₂O₅ were experimentally obtained under conditions similar to Kasakov's conditions.

Therefore, KAZAKOV's theory is rejected but at the same time, KAZAKOV's view of upward current is still employed in the discussion of enrichment of seawater phosphorous. On the other hand, experimental work conducted by AMES (1959) in (BENTOR, 1980) shows the successful transfer of calcite to apatite. This theory is refuted based on unsuitable experimental conditions (1.5 gm/l phosphorous content and 11.0 pH value) for the deposition of phosphorites from seawater, and the absence of any sign of phosphatization of limestone exposed to seawater (BATURIN, 1982).

The role of clay minerals in phosphorous fixation is reasonably referred and discussed in many literatures. The organic materials rich with organism remains is accumulated at seafloor mud, where oxidation and decay take place which led to the liberation of HPO₄²⁻ a form of dissolved phosphorous. The seafloor mud constituents of clay minerals (illite, smectite, vermiculite) act on fixation the dissolved phosphorous and the amount of P-fixation increase with the increase in pH. Later, the fixed phosphorous is bonded to calcium forming the apatite phase (STAMATAKIS & KOUKOUZAS, 2001). Other fixed phosphorous bonds to aluminum and iron forming amorphous phases (x-orthophosphate complexes) within apatite.

The study of MORE (1969) in (BATURIN, 1982) suggested the role of residual charge on phosphate colloidal particles in the extraction of seawater phosphorous and the formation of phosphate nodes, whereas RUTTENBEREG & BERNER (1988) in (TRIBBLE *et alii*, 1995) suggested the trapping of seawater phosphorous and form apatite as a coating around the clay mineral particles. KNUDSEN & GUNTER (2002) suggested that for large scale phosphorites to form, two major obstacles must be overcome; first, P must be concentrated from 1 to 2 million times in seawater, and secondly, phosphate (PO₄) must be accumulated and francolite must crystallize.

Although many different mechanisms were suggested, yet no single one can explain the deposition of thick beds of phosphorites deposited in the shallow marine environment, moreover, the environmental conditions of the suggested mechanisms were narrow in range and only applicable to phosphorites of limited location. Therefore, the suggested mechanisms are short of general application, yet it represents a single stage in the process of an increase in phosphorous content. For example, the phosphate sediments of Peru-Chile at the layer of low oxygen is associated with the strong activity of upwelling currents and with planktonic blooms

(BRASIER, 1980). Therefore the attention was redirected to organic activity induced by an organism in the discussion of seawater phosphorous enrichment mechanism (CAYENX (1959) in (SLANSKY, 1986) which received less attention in the past due to lack of the necessary data.

The role of organic material in the phosphorous enrichment can be shown through the ability of various species of organisms on trapping seawater phosphorous and enrichment within soft organic materials (and some in hard parts) as in phytoplankton (SLANSKY, 1986; STAMATAKIS & KOUKOZAS, 2001) and in Phycophyta, Cyanophyta and diatoms algae (BORTONE *et alii*, 1996; SLANSKY, 1986), also in pseudomonas fluorescent bacteria and in flagellates (XIAO & KNOLL, 2000), teeth, bones and skeleton of a large organism like fish. Upon death and bacteria decay activity, the organisms remain liberates phosphorous to the seawater and more enrichment rate is expected in interstitial water within the seafloor sediments and forming the phosphate phases.

THE STUDY AIMS

The study aims to discuss the mechanism of raising the small concentration of phosphorus from sea water to high concentrations in phosphate rocks, factors that led to the formation and distribution of marine phosphate deposits in the areas of the continental shelf, the mechanism of formation of francolite mineral in phosphorite depending on the distribution of elements in the crystal structure, and develop a sedimentary model for the concentration and formation of phosphates.

MATERIALS AND METHODS

Thirteen samples of Akashat phosphorite were analyzed by X-ray diffraction technique in General State of Geological Survey and Mining-Baghdad and University and O'rlans University-France, for mineralogical analysis. Both labs use $\text{Cu}\alpha$ radiation, Ni filter, 30 mA and 40 kV, background intensity (100 count/sec). The differences between the two labs are in the intensity scales (2000 and 4000) count/sec and chart velocity (1 cm/2 θ and 0.5 cm/2 θ), respectively.

Twenty-three concentrated apatitic rock samples were analyzed by X-ray fluorescence technique for chemical analysis of major oxides and Sr in the X-ray Unit in Department of Geology-University of Mosul, according to the standard conditions for analysis (JEFFERY & HUTCHISON, 1981), using instrument type PHILIPS, PW.1450/10, Cr tube, 40 Kv, 30 mA, in vacuum path and counting in 20 sec.

RESULTS AND DISCUSSION

Mechanisms of P-enrichment and phosphorite formation

No single mechanism may claim the P-enrichment within the marine environment (TRIBBLE *et alii*, 1995). The increase

of seawater P-concentration (70-75) ppb to about 30 wt% in phosphorites required more than one stage associated with one or more enrichment mechanisms of biological, chemical, mechanical (ABDEL-RAHMAN, 1992; FILIPPELLI, 2011) or combined of all which participate in P-enrichment required for the formation of P mineral phases and phosphorites deposition.

The following discussion declares the stages of P-enrichment:

1. Biological Trapping Of Seawater Phosphorous

Phosphorous is one of the major essential elements for living cell and it is included as organic compounds (DNA & RNA). The P_2O_5 content (dry weight) in a non-skeleton organism like Diatom 3%, flagellates 3% algae 3.7% and reach up to 7% in bacteria and planktons. Phosphorous minerals also present within teeth tissues and skeleton bone of large organisms, where P_2O_5 content may reach as high as 40% in fish bones (SLANSKY, 1986). From the preceding discussion, it appears the role of seawater P capturing and enrichment by a range of living organisms from micro-size (the plankton) through to large size like fish. This mechanism is very important in the accumulation of sea water-dispersed phosphorous in a limited space, i.e. living organism which finally died and their remains accumulated on the seafloor.

2. P-enrichment by decay

When marine life dies during its life cycle, or as a result of mass death due to a sudden change in life conditions (physical and chemical such as temperature and salinity), or by the influence of volcanoes (LUCAS & PREVOT-LUCAS, 2000). Later, the fallen dead remains accumulated at the seafloor and buried within upper muddy sediments, where the soft parts were subjected to bacterial decay under anaerobic conditions (BORTONE *et alii*, 1996; MCARTHUR, 1980), which result in the formation of organic compounds like kerogen and humic compounds (BENALIOULHAJ *et alii*, 2000) within interstitial water below seawater/floor sediments interface. The buried organic compounds are enriched with phosphorous and show stability under an anoxic environment. The buried hard parts like teeth and skeleton bone remains were decayed by the action of specific bacteria in the floor mud. This also favors the enrichment of phosphorous in interstitial water. Both the soft and hard parts do not liberate phosphorus and no phosphorous compounds were formed above the water/sediment interface. The dahlite phase of the hard parts (bones and teeth) may convert to Francolite above this boundary.

The decay of soft and hard parts of the organism is accompanied by the disintegration of carbonates skeletons which often form of aragonite (FOUNTAIN & MCCLELLAN, 2000) through the action of specified species of bacteria (BATURIN, 1982; LUCAS & PREVOT-LUCAS, 2000) and this may participate in calcium and carbon enrichment in interstitial water. The degree of enrichment of interstitial water with phosphorous, calcium and

carbon depend on the activity of the relevant bacteria (LUCAS & PREVOT-LUCAS, 2000). It is worth mention here, that the volcanic activities participate in the formation of iron-manganese nodules (COMPTON *et alii*, 2000), which often adsorbed phosphorous, and on burial environment where ferric converted to ferrous that led to the liberation of phosphorous and its enrichment in interstitial water. In the case of weak submarine volcanic activity and low rate of formation of iron-manganese nodules, the organic activity of increasing the phosphorus content of the interstitial water is the most effective. The formation of calcium phosphate compounds in sediment pores, require an increase of P content to appropriate values, which make calcium in equilibrium with phosphate phases, not with carbonate phases and this required a decrease in Mg/Ca ratio to optimum value to ensure the continuation of the process (O'BRIEN *et alii*, 1990). The presence of Mg reduce 20 times the growth rate relative to the case of the absence of Mg because it occupies sites on calcium phosphate halts its growth (BENTOR, 1980). Organic material participates in decreasing the Mg/Ca by calcium enrichment in sediment pores (BATURIN, 1982) and trapping of Mg by clay minerals rich in Mg like palygorskite and sepiolite through the exchange of Mg between pores water and clay minerals (BENTOR, 1980) and also with carbonate minerals to form dolomite. The enrichment of interstitial water with P and Ca led to precipitation of gelatinous calcium phosphate (BATURIN, 1982; SLANSKY, 1986). The presence of fluoride in sediment pores favors the formation of apatite or formation of gelatin calcium phosphate compounds. This stage reflects the role of biochemical in the formation of calcium phosphates.

3. Reverse fluxing stage

This stage represents the reverse reflux of phosphate from sea floor sediment to overlying seawater, and this is an important part of the marine phosphorous cycle. The reverse reflux occurs in two modes: the first mode is the liberation of phosphate in the form of HPO_4^{2-} from floor sediments to seawater, as a results of the dissolution ability of gelatinous calcium compounds (BATURIN, 1982; SLANSKY, 1986) and the decreasing in pH values, because of increase in CO_2 partial pressure at depth, favors the dissolution of calcium phosphate and apatite, which exposed at seafloor as a result of biological activity or movements of floor sediments (MCARTHUR, 1985; TRIBBLE *et alii*, 1995). The second mode includes the physico-chemical effects of marine current led to exposure and fragmentation of phosphate compound (not affected by dissolution) to finer particles and later subjected to winnowing (TRIBBLE *et alii*, 1995).

4. Upwelling currents stage

The variation in density and temperature of sea water layers activates the occurrence of marine upwelling currents which move upward along the continental slope of the hot-warm region

of low latitude. The upwelling currents play a major role as a carrier and an efficient agent of transportation of dissolved and winnowed fine particles of phosphate phases up to the continental slope where it accumulated and deposited (AL-SHEREIDEH *et alii*, 2010; COMPTON *et alii*, 2000; FOUNTAIN & MCCLELLAN, 2000). The transportation of phosphate phases at depth (where it formed and up to the continental slope where it accumulated and deposited) is often not a long journey. For example, the phosphate phases traveled a distance of only 200 m at the Namibia coastal region (BENTOR, 1980). The importance of upwelling currents is reflected in the drawing of world phosphorites distribution as in the case of the southern side of the Tethys sea where phosphorites of the middle east and north Africa and up to Columbia are found (DIONE *et alii*, 2018; PUF AHL *et alii*, 2003). The upwelling current cause phosphorous enrichment at the upper continental slope area and biota flourishing like planktonic and algae blooms. The thickest deposits are amalgamated/condensed beds reflect the variations in upwelling intensity and storm frequency through the time (SIMANDL *et alii*, 2012).

5. The phosphatic phases formation stage

The P-pouring by upwelling currents results in the flourishing of marine organisms at the shelf to the slope of continents. This reflected by the accumulation of organism remains including foraminifera, radiolarian, diatomsetc (LUCAS & PREVOT-LUCAS, 2000) and bone and skeleton remain of larger organisms like fish within the upper (15-18) cm of the floor mud (O'BRIEN *et alii*, 1990). On burial, different bacteria act on the decay of soft and hard parts of organisms and this leads to an oxygen-depleted environment. Therefore, pores water conditions are dyoxic-anoxic (LUCAS & PREVOT-LUCAS, 2000) which is not related to seawater composition only, but the combined influence of both sea and interstitial water. The interstitial water is enriched with P, Ca, and C as a result of organism decay, whereas S, Na, LREE, U, and Y are related to the chemistry of seawater (BARBARAND *et alii*, 2003; MCARTHUR, 1985). This mixed enrichment results in the formation of amorphous intermediate phases (di-, tri- and octa-calcium phosphates) before the formation of proper apatite (ANN *et alii*, 1999). Seafloor sediments enriched with phosphate phases are called phosphatic mud.

The formation of phosphate phases reflects direct precipitation from interstitial water below the seawater/sediment interface. Such process of precipitation is not possible above this surface for reasons related to decreasing in Mg/Ca ratio and reasons concerning the stability of environmental conditions (temperature, CO_2 partial pressure, and pH) necessary for apatite precipitation as stated by KAZAKOV (1937) in (BENTOR, 1980), during relatively long geological time. On the other hand, the association of limestone with phosphorites depends on the variation in the availability of material produced by organism

decay. As the precipitation of phosphorites is related to the role of organic water below sediment/water surface, the precipitation of carbonate depends on the abundance of other types of organic material which upon decay, produce carbonate ion above sediment/water interface. In general, the source of carbonate ion is the skeleton of marine organisms and shells of calcitic and aragonitic compositions (LUCAS & PREVOT-LUCAS, 2000) with high porosity and permeability and no sea water saved in such accumulation. Whereas the same accumulation but with fine size sediment of porosity and low permeability may save seawater enrichment with phosphate, which reacts with host sediment or directly precipitate phosphate phases. The alternation of phosphorites with limestone is related to variation in chemical and physical conditions as well as in seawater level changes. It is a widely held view that phosphorites deposition is related to transgression (RIGGS *et alii*, 2000) while the deposition of carbonate sediment is associated with seawater regression (AL-BASSAM, 1992).

6. Diagenetic process stages

Diagenesis affect to a great extent the formation of Francolite and phosphate constituents and their distribution in phosphorites (BATURIN, 1982). The diagenesis stage includes the petrological, mechanical, chemical and biological processes of diagenesis which increased in activities at a low deposition rate (TAYLOR & MACQUAKER, 2000). Diagenesis participate in a different form and a various degree at different stages leading to the sorting of phosphate constituents and its re-formation. Diagenesis at sedimentary environments of continental shells is affected by various conditions: physical (includes movement of marine currents, sea waves, energy level, temperature, and salinity), chemical (represented by the concentration of fluoride, trace elements, elements related to clastic constituents and cations exchanged with francolite) and biological (related to type and abundance of organic material, type of the associated bacteria and variation in biological conditions). This is reflected by the diversity and distribution of phosphate grains within the phosphorites facies (INGALL *et alii*, 1990). In the following is a brief account of the different diagenetic process:

a. Petrological diagenetic processes:

These processes primarily include the lithification of phosphatic mud and the formation of microspherule (RIGGS *et alii*, 2000) through specific changes of remains of bones and organism skeleton with alteration of phosphate phases and the association of non-phosphate minerals like carbonate and clay minerals in phosphate sediments, in addition to variation in environmental conditions affecting the type of cementing material.

The reworking represents a great part of the petrological diagenetic process (OBERLINDACHER & ROBERTS-TOBEY, 2002),

as re-distribution of the phosphate constituents was achieved through exposed reworking process which includes re-composing with regards to shape, size, type, composition, and mineralogy. An example of consequences of reworking is the formation of pellets from microspherule at a quiet and low energy environment and the exposure of phosphatic mud to reworking at an environment of fluctuating energy (OBERLINDACHER & ROBERTS-TOBEY, 2002). where intraclasts are formed (RIGGS *et alii*, 2000), and in case of strong reworking which led to the formation of non-organic pellets (SOUDRY & NATHAN, 1980). During lithification: the form and texture of teeth and bone were preserved, the crystallization of amorphous phosphate phases to Francolite, mineralization of organic material within phosphate constituent as in the case of coprolite and filling chamber of foraminifera tests with phosphate constituents.

b. Mechanical diagenetic processes:

The microspherule and coprolite were reduced in size through breaking, fissuring, and parting. The fine size product was transported by the action of marine currents and sea waves and led to re-distribution of phosphate constituents in the sedimentary basin. The shallow and high energy environments favor the formation of phosphatic oolites (TRAPPE, 2001) and winnowing results in the transportation of phosphatic constituents from a location where it formed to the host sediments in the continental shelf. Marine storms participate in re-distribution and reworking of primary phosphate facies leading to the formation of granular phosphorites (FILIPPELLI, 2011; PUFAHL *et alii*, 2003). The limited movement of floor sediments result in a partial environment of phosphate materials, through the separation of fine grains from heavy apatite grains (BENTON, 1980), and this led to the formation of friable and well-sorted phosphatic sediment with little cementing material and clay-carbonate matrix (GALLALA *et alii*, 2016).

c. Chemical diagenetic processes:

Diagenesis affects the formation of Francolite through variation in element distribution within the crystal structure. The extraction and fixation of fluoride in the crystal channels lead to the conversion of amorphous phosphates phases of the phosphate mud to crystalline Francolite (BATURIN, 1982). During diagenesis stages, the variation in chemical conditions is reflected in the replacement of Ca(II) site by the element (Na, Mg & HREE) in solution (LANFRANCO *et alii*, 2004). This explains the variation in the content of such elements in francolite. The formation of organic complexes with some trace elements may share the explanation of Francolite enrichment with those elements. Phosphatization process is considered as the reaction of HPO_4^{2-} phase with the Ca of the dissolved carbonates under conditions of the low value of pH (GUIDRY &

MACKENZIE, 2003; TRIBBLE *et alii*, 1995).

This is accomplished by the decay process within the concept of demineralization/remineralization. The carbonate cement is exposed to the reaction with HPO_4^{2-} phases leading to the formation of phosphatic cementing materials.

d. Bio-diagenetic processes:

The organic materials and the associated living bacteria share in the enrichment of phosphate around the phosphatic grains (SOUDRY, 2000), in addition to organic material within the phosphatic grain like peloids where environmental conditions range from anoxic to suboxic. Upon oxidation, bacteria faced destruction and liberates HPO_4^{2-} which combined with calcium forming amorphous calcium phosphate (Cellophane) envelops or clouds around phosphatic grains. This represents stages in the direction of the formation of francolite with continuous diagenesis where conversion to crystalline francolite was achieved as a result of fluoride extraction (PUCÉAT *et alii*, 2004). Therefore, the organic materials and bacteria share in the process of preferential growth of phosphatic grains. The fecal, peloids and coprolite appear harder and darker in color because of their higher content of organic materials and cellophane.

7. The depositional environment within the continental shelf

The continental shelf (outer and inner) and the upper continental slope represent the area associated with biota plumes, hence, the deposition of phosphorites (RIGGS *et alii*, 2000) in different environments such as isolated, near the coast, high energy and temperance energy environments (Fig. 4). Such variation in depositional environments led to different phosphorites facies, for example, the depositional of ooidal phosphorites facies reflect shallow, near the coast and high energy environment within inner continental shelf (DIONE *et alii*, 2018;

VAN HOUTEN, 2000), whereas, the peloidal phosphorite facies reflect the outer shelf and low energy environment (AL-BASSAM, 1992; SOUDRY & NATHAN, 1980) and coprolite phosphate facies on the hard ground represents the shallow environment affected by the activities of a basinal organism (horizontal burrowing and boring) (AL-BASSAM, 1992).

The depositional environment in the continental shelf, contribute to the distribution of phosphate constituent, in addition to presence of other factors that explain the variation of mineral content, such as burial depth, age, and weathering, as evidenced by the transformation of francolite to fluorapatite with the time (MCARTHUR, 1985; TRIBBLE *et alii*, 1995). Weathering contributes to the alteration of some phosphate minerals to carndalite, vivianite, and wavelite minerals. Although Francolite is the most stable sedimentary phosphate mineral in the marine environment (BENTOR, 1980) yet the chemical conditions of the diagenetic process led to variation in the chemical composition of the minerals (TRIBBLE *et alii*, 1995) and the formation of phosphate phases, some of which, associated with the water of deposition environment and with detrital elements provided by river inlets (MCARTHUR, 1985). Such phases are not common and associated with the nature of the sedimentary basin and variation in properties from one place to another.

According to the above conceptions, the study presents a model (Fig. 4) of the all expecting mechanisms to form phosphorites at least in the area among the middle east on the southern coast of Tethys sea.

FRANCOLITE FORMATION OF THE MIDDLE PALEOCENE PHOSPHORITES

The mineralogical analysis by XRD technique shows that Francolite is the main phosphate mineral in middle Paleocene phosphorite, in addition to the small amount of calcite and traces

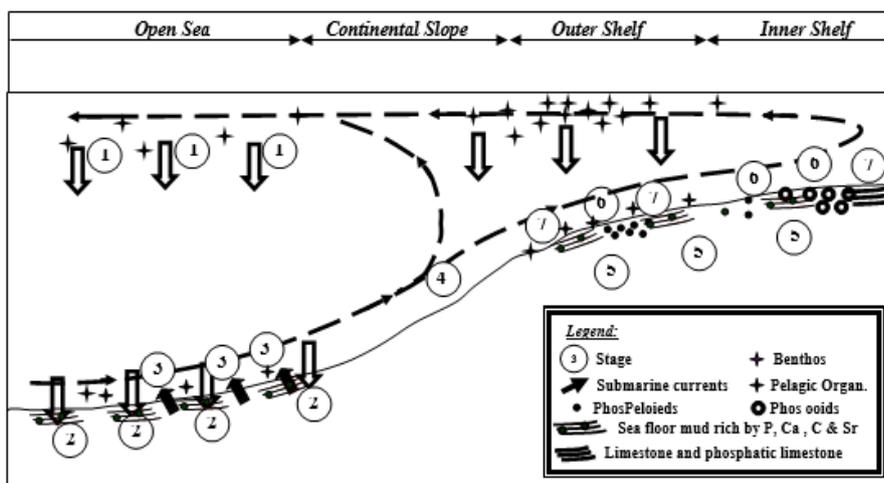


Fig. 4 - Model of Mechanisms of P- enrichment and phosphorite formation

of dolomite, quartz, gypsum, and palygorskite (Fig. 5 and 6). The presence of the collophane phase which not shown in XRD reflections results in broad reflections of large width at the half-height at low d-spacing of the diffractograms. This led to an overlap of 211, 112, 300 and 202 reflections (Fig. 5).

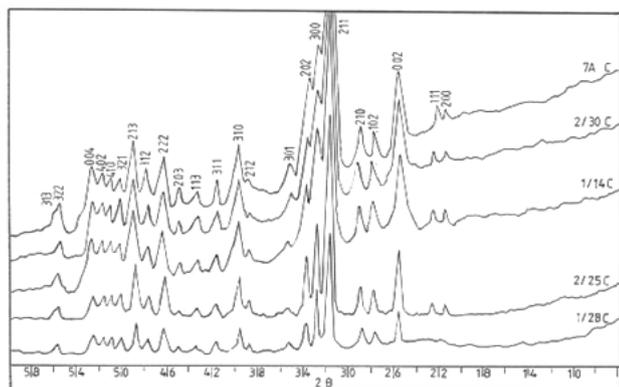


Fig. 5 - The XRD diffractograms of francolite in Akashat phosphorites

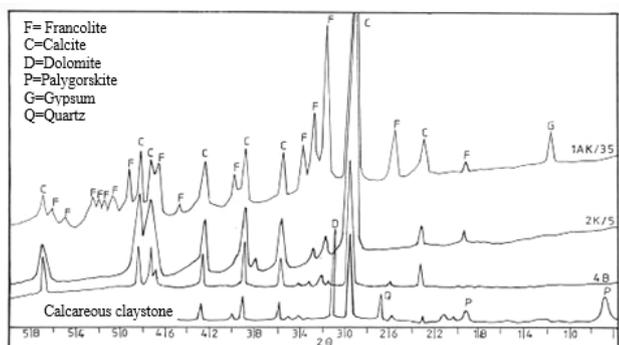


Fig. 6 - The XRD diffractograms of Akashat phosphatic limestones

The presence of apatite and collophane phases reflect the abundance of peloids, ooids, and phosphorolites, in addition to phosphatic cementing. Crystal d-spacing of the recorded reflections of most samples show values range between those of fluorapatite and carbonate-apatite but inclined to the values of fluorapatite (Table 1). The last note may signals that the carbonate replacement in fluorapatite structure leads to the formation of carbonate fluorapatite (Francolite) at an earlier stage of phosphorite deposition (TRIBBLE *et alii*, 1995). Francolite is less stable relative to fluorapatite, where diagenesis, weathering and geological time may bring changes in chemical composition and crystal structure in the direction of fluorapatite formation (MCARTHUR, 1985; MCCLELLAN, 1980).

The present study agrees with the view of phosphate replacement by carbonate + fluoride ions (MCCLELLAN, 1980) because of two reasons: first, the view includes replacement of phosphate tetrahedron by pseudo-tetrahedron of both $CO_3^{2-} + F^-$,

and second, the replacement of $CO_3^{2-} + F^-$, with total charge -3, for phosphate (PO_4^{3-}) fulfill the charge balance (JIANG *et alii*, 2020). This implies that no need for sodium replacement for calcium as suggested by MCCONNELL (1973) in (MCCLELLAN, 1980) and there is no relation noticed between Na_2O/P_2O_5 with carbonate replacement in the present study. Phosphate replacement by carbonate results in decreasing *a*-axis and slightly increased in the *b*-axis (LIM & GILKES, 2001). The length of (*a*) can be used for the estimation of the carbonate content of Francolite (Table 2). Other studies used 004 reflections which appear broad and low intensity in the present study. Instead, it is suggested here to use the differences in angle distance of 310 and 002 reflections and 002 and 310 reflections (AL-YOUZBAKEY *et alii*, 2002). It seems that the best fit of *a*-axis length is related to the difference in angle distance of 002 and 310 reflections:

$$a = -0.0682 * \Delta 2\theta_{(002-310)} + 10.321 \dots\dots\dots(1)$$

Selected values of *a*-axis lengths and the proportion of carbonate (%) from several international and local published analyzes (Fig. 7) (AL-YOUZBAKEY, 2004), lead to inference a relation between aA° & $CO_3\%$:

$$CO_3\% = -105.66 a + 990.76 \dots\dots\dots(2)$$

{Table 3, column 1}

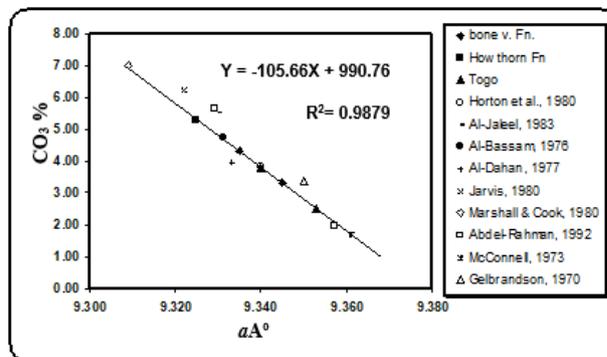


Fig. 7 - The relationship between *a* – axis length and the C mole/formula in francolite from published data in (AL-YOUZBAKEY, 2004)

The two equations (1 & 2) were combined in one equation (3) to be used in the calculation of carbonate content in francolite in mole/formula, from the angle distance difference of 002 and 310 reflections as in the following:

$$CO_3(mole/formula) = 1.441 * \Delta 2\theta_{(002-310)} - 19.951 \dots\dots\dots(3)$$

{Table 3, column 2}

The present study depends on the relation between *a* & *c* A° , the *a/c* ratio and the CO_3 substitution in Carbonate-apatite

PHOSPHORUS CONCENTRATION MECHANISMS AND PHOSPHORITE FORMATION, CASE STUDY: THE FORMATION OF FRANCOLITE IN AKASHAT PHOSPHORITE OF EASTERN TETHYS, IRAQI WESTERN DESERT

Crystal faces <i>hkl</i>	Fluorapatite ⁽¹⁾		Carbonate-apatite ⁽²⁾		Studied samples (2K/24) ⁽³⁾		Studied samples (2K/25 Con.) ⁽³⁾	
	<i>d-spacing</i>	<i>I / I⁰</i>	<i>d-spacing</i>	<i>I / I⁰</i>	<i>d-spacing</i>	<i>I / I⁰</i>	<i>d-spacing</i>	<i>I / I⁰</i>
002	3.442	40	3.460	25	3.456	50	3.45	50
102	3.167	14	3.170	2	3.184	16	3.173	16
210	3.067	18	3.040	10	3.061	20	3.061	20
211	2.800	100			2.79	100	2.799	100
112	2.772	55	2.78	100	2.777	60		60
300	2.702	60	2.680	40	2.700	50	2.700	50
202	2.624	30	2.622	10	2.623	30	2.627	30
310	2.250	20	2.231	16	2.244	24	2.247	24
221	2.218	4			2.215	7		7
311	2.140	6	2.124	2	2.133	7	2.132	7
113	2.061	6	2.069	2	2.058	7	2.063	7
222	1.937	25	1.929	16	1.935	25	1.934	25
312	1.884	14	1.858	10	1.886	10	1.881	10
213	1.837	30	1.838	16	1.838	30	1.838	30
321	1.797	16			1.794	11	1.791	11
410	1.771	14	1.783	10	1.774	15	1.770	15

(1) Fluorapatite: $a = 9.368 \text{ \AA}$, $c = 6.884 \text{ \AA}$. } data from Brindley & Brown (1980).
 (2) Carbonate-apatite : $a = 9.309 \text{ \AA}$, $c = 6.927 \text{ \AA}$. }
 (3) selected samples from the 13 studied samples.

Tab. 1 - The *d-spacing* (\AA) and intensity for the crystal faces in fluorapatite, carbonate-apatite, and Akashat apatite

Samples	$a\text{\AA}$	$c\text{\AA}$	c / a	$V \text{ \AA}^3$	$\Delta 2\theta_{002-300}$	$\Delta 2\theta_{002-310}$	$\Delta 2\theta_{004-410}$
1AK/16	9.333	6.905	0.7396	521.62	7.4	14.4	1.55
1AK/25	9.336	6.904	0.7395	521.11	7.49	14.47	1.25
2K/24	9.338	6.895	0.7384	520.77	7.27	14.35	1.27
1S 15	9.336	6.900	0.7395	521.16	7.48	14.44	1.17
11B	9.337	6.906	0.7396	521.36	7.43	14.4	
NL1	9.336	6.901	0.7380	520.06	7.34	14.33	NL1
1AK/14 Con.	9.340	9.901	0.7389	521.32	7.27	14.33	1.63
1AK/28 Con.	9.336	6.902	0.7393	520.93	7.45	14.5	1.23
2K/25 Con.	9.342	6.900	0.7386	521.54	7.35	14.3	1.45
2K/30 Con.	9.333	6.904	0.7395	521.78	7.36		1.38
7A Con.	9.336	6.906	0.7398	521.82	7.26	14.3	1.4
Teeth 1	9.357	6.890	0.7363	522.43	7.25	14.13	1.58
Bone 1	9.351	6.890	0.7367	521.77	7.33	14.33	1.48
F-Apatite	9.368	6.884	0.7348	523.20	7.26	14.18	1.58
C-Apatite	9.309	6.927	0.7441	519.86	7.68	14.67	1.49

Tab. 2 - XRD parameters of Akashat francolite

samples	CO ₃				Add. F	Na	Mg
	1	2	3	Ave.			
1AK/16	0.93	0.80	0.93	0.89	0.55	0.23	0.09
1AK/25	0.87	0.90	0.83	0.87	0.52	0.23	0.08
2K/24	0.81	0.73	0.75	0.76	0.30	0.19	0.07
1S 15	0.86	0.86	0.82	0.85	0.42	0.22	0.08
11B	0.85	0.80	0.81	0.82	0.57	0.21	0.08
NL1	0.87	0.70	0.84	0.80	0.45	0.21	0.08
1AK/14con.	0.79	0.70	0.72	0.74	0.45	0.19	0.07
1AK/28con.	0.87	0.95	0.84	0.88	0.46	0.23	0.09
2K/25con.	0.73	0.66	0.65	0.68	0.42	0.17	0.06
2K/30con.	0.93	0.99	0.93	0.95	0.52	0.25	0.09
A7con.	0.87	0.66	0.84	0.79	0.58	0.20	0.08
Aver.				0.82	0.48	0.21	0.08

Tab. 3 - The mole proportion of CO₃, additional F, Na and Mg (mole/formula) in francolite formula from XRD analysis

and fluorapatite to estimate the $CO_3(\text{mole/formula})$ from $a A^\circ$, as in the following:

$$CO_3(\text{mole/formula}) = 123.69 a^2 - 2338.7 a + 11054 \dots\dots\dots(4)$$

{Table 3, column 3}

The study declare that there is no relation between additional F which calculated from chemical analysis and a -axis, but it found a linear relationship with a c -axis to estimate the additional F (Table 3) as follows:

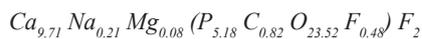
$$F_{add}(\text{mole/formula}) = 24.751 c - 170.36 \dots\dots\dots(5)$$

MCCLELLAN & LEHR (1969) found two relations for calculation of Na and Mg as a function of the mole proportion of CO_3/PO_4 , as follow:

$$Na = 1.333 * CO_3/PO_4 \dots\dots\dots(6)$$

$$Mg = 0.5 * CO_3/PO_4 \dots\dots\dots(7)$$

The X-ray diffraction parameters incapable of estimating the accurate chemical formula of francolite due to substitution of many elements in crystal structure which is not detected in X-ray parameters. But it could help to estimate the common ions like CO_3 , F, Na, and Mg, and according to this information it is possible to coin the chemical formula of francolite:



GEOCHEMISTRY

As mentioned before, the interstitial water is enriched with phosphate associated with hummus and kerogen compounds liberated from bacterial decay of organic material. The liberated phosphate combined with dissolved calcium resulted from seawater mixing and disintegration of hard parts of the calcitic and aragonitic composition. It is safe to say that P, Ca and Sr elements are associated with organic activities of the decay bacteria in the interstitial water, while Na, S, U, Y, and LREE represent seawater imprints left in the interstitial water. Sodium and sulfate are bounds to the crystal lattice through the replacement of calcium and phosphate respectively. The low mole fractions of sodium and sulfate indicate that alkalinity and salinity of seawater were just above normal values (AL-BASSAM, 1992) of francolite to be formed in the shallow continental shelf, where sometimes exposed to partial isolated from the open sea by local submarine bars.

Trace element distributions within francolite show that the concentration of calcium and related elements depends on their ability to occupy both calcium sites (I&II). Uranium (U^{4+}) occupies both sites at reducing conditions and because of its additional preference for Ca(II) site, Uranium concentration doesn't precisely

reflect the geochemistry of marine water (JIANG *et alii*, 2020). The absence of iron-manganese relation precludes any significant activity of submarine volcanism and this leads to the conclusion of the absent role of iron-manganese in phosphorous enrichment at Akashat reducing basin of deposition. As a result of the anoxic-suboxic basin, francolite of Akashat phosphorite is enriched with Ce occupied (with other LREE) the site Ca (I), ($Ce_{(anomaly)}$): Min. = 0.01, Max = 1.98 and Mean = 0.6 for 24 studied samples) (AL-YOUZBAKEY, 2004). Whereas francolite and seawater are depleted in Eu.

The enrichment of interstitial water with carbon is associated with the decay process of organic materials. Carbon replacement within francolite is taken as a measure of the warm temperature of the water and a pH little bit above the normal value which is required for francolite formation. Carbonate replacement within francolite occurs during lithification and at the beginning of the early diagenetic process. The data of the present study shows a lower carbonate mole fraction of francolite and it can be explained by the repeated exposure of Akashat francolite to the chemical diagenetic process which leads to a more stable phase of fluorapatite (MCARTHUR, 1985, 1980; TRAPPE, 2001). It is possible to estimate the loss of carbonate by the action of the diagenetic process, through the calculation of carbon mole fraction within the chemical formula of francolite unit cell as follows:

$$\text{Max } C(\text{mole/formula}) \text{ in francolite} - C(\text{mole/formula}) \text{ in Akashat francolite} / C(\text{mole/formula}) \text{ in Akashat francolite} = (1.8-0.91)/0.91 = 0.98;$$

(1.8-0.91): represent the lost $C(\text{mole/formula})$ in Akashat francolite due to the diagenetic processes;

0.91: $C(\text{mole/formula})$ in Akashat francolite calculated from the concentrated apatite.

The smaller ionic size of Mg led it to occupy the Ca(II) site in francolite. The low Mg content reflects the low supply of detritus materials, as well as the distribution of Mg among palygorskite, sepiolite, and dolomite. The organic materials participate in picking up and fixation of some elements like As, Pb, V and HREE on the phosphatic grains through the accumulative growth stages by the bio-activity of bacteria. The biogenic-diagenetic processes of phosphorite formation control the distribution of elements in francolite by substitution, absorption and/or adsorption in the Ca(II) site, the middle crystal channel and on the phosphatic grain surfaces.

Depending on the average mole/formula of the elements in the crystal structure of Akashat francolite mentioned in Tables (4 & 5), the chemical formula is:



Oxides & Elem.	Concentrated apatite samples												
	1AK/14	1AK/16	1AK/24	1AK/25	1AK/28	1S/0	1S/7	1S/10	1S/15	2K/19	2K/24	2K/25	2K/28
SiO ₂	1.30	1.40	1.58	1.46	1.35	1.21	1.39	1.67	2.48	1.72	1.44	1.86	1.17
Al ₂ O ₃	0.23	0.25	0.09	0.08	0.06	0.04	0.25	0.30	0.16	0.12	0.06	0.11	0.04
Fe ₂ O ₃	0.06	0.05	0.07	0.06	0.05	0.04	0.09	0.07	0.23	0.14	0.05	0.08	0.05
MgO	0.32	0.15	0.20	0.12	0.29	0.33	0.32	0.54	0.35	0.17	0.23	0.35	0.21
CaO	51.41	51.27	50.55	51.27	52.77	53.22	50.10	50.58	52.76	50.32	53.53	51.73	53.90
K ₂ O	0.01	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.01
Na ₂ O	0.41	0.35	0.49	0.53	0.46	0.28	0.36	0.44	0.40	0.41	0.35	0.04	0.19
P ₂ O ₅	32.50	31.86	32.58	31.24	32.88	32.88	32.34	32.67	33.76	32.13	35.00	32.70	34.91
F	4.15	4.42	3.64	4.34	4.17	4.64	3.37	3.30	3.67	3.96	3.97	3.96	3.84
Cl	0.06	0.05	0.06	0.06	0.06	0.05	0.08	0.06	0.07	0.05	0.05	0.05	0.06
SO ₃	1.57	1.47	1.88	2.01	1.77	1.21	1.84	1.77	2.12	1.47	1.02	0.90	1.18
Sr	1687	1598	1765	1545	1325	2020	2664	1745	1738	1584	1367	1392	1200

Oxides & Elem.	Concentrated apatite samples										Min.	Max.	Aver.
	2K/30	7A	11B	BH7	BH9	BH10	100/2K	100/3K	OL143	L160			
SiO ₂	1.52	1.41	1.30	1.40	1.21	1.26	1.90	2.22	2.00	2.09	1.17	2.48	1.30
Al ₂ O ₃	0.24	0.27	0.24	0.07	0.22	0.26	0.29	0.11	0.32	0.32	0.04	0.32	0.23
Fe ₂ O ₃	0.05	0.06	0.07	0.07	0.07	0.06	0.14	0.15	0.13	0.09	0.04	0.23	0.06
MgO	0.30	0.32	0.45	0.09	0.31	0.37	0.18	0.18	0.19	0.17	0.09	0.54	0.32
CaO	52.42	49.60	51.84	50.20	50.03	49.74	49.15	50.79	50.52	49.98	49.15	53.90	51.41
K ₂ O	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.02	0.01
Na ₂ O	0.18	0.31	0.48	0.29	0.16	0.51	0.24	0.22	0.31	0.27	0.04	0.53	0.41
P ₂ O ₅	32.86	30.53	33.31	31.06	30.00	30.85	30.17	32.03	31.62	31.07	30.00	35.00	32.50
F	4.31	4.26	4.27	3.97	4.51	4.07	3.92	3.60	3.85	4.33	3.30	4.64	4.15
Cl	0.05	0.06	0.06	0.06	0.06	0.06	0.07	0.08	0.07	0.06	0.05	0.08	0.06
SO ₃	1.14	1.35	0.96	1.48	1.29	1.36	1.46	1.99	1.36	1.31	0.90	2.12	1.57
Sr	1727	1618	1530	1834	1840	1593	1632	1513	1438	1516	1200	2664	1687

Tab. 4 - The concentrations of major oxides (wt%) and trace elements (ppm) in concentrated apatitic grains

Elem.	Ca	Na	Sr	Mg	P	S	C	F	O	F	Cl
Min.	9.75	0.01	0.01	0.00	4.72	0.12	0.72	0.29	22.96	1.99	0.01
Max.	9.96	0.18	0.03	0.08	5.07	0.28	1.04	1.04	23.71	1.99	0.01
Aver.	9.84	0.12	0.02	0.05	4.89	0.20	0.91	1.74	23.26	1.99	0.01

Tab. 5 - The mole/formula of ions in the unit cell of francolite from chemical analysis of concentrated apatite grains

DEPOSITIONAL ENVIRONMENT OF PHOSPHORITES IN AKASHAT FORMATION

The succession of facies of phosphorites (industrial rocks) is displayed in Fig. 3. It is started with a bed of one-meter thickness which represents the facies of Calci-Phos. Ooidal Phosphorite. It is overlain by three zones of alternation of phospeloial phosphorite facies with phosphatic limestone facies which make all together 2-2.8 m thickness. It followed upward by phospeloidal phosphorite facies, phosphatic peloidal wackestone facies (or phosphatic lime mudstone facies), calci foraminiferal peloidal phosphorite facies, calci peloidal phosphorite facies, and calcicortoid peloidal phosphorite facies and the overall thickness amount to (5.5-7.5) m The whole succession overlay by overburden rocks. The

succession of the phosphorites and associated rocks reflect the condition of depositional environments regards to condition variation of burial depth, water energy, the influence of marine currents, biological prosperity and the basin location within the marine environment (Fig. 8).

The shelly limestone facies is located below the phosphorite succession and reflects shallow water condition of high energy of sedimentation at the inner-shelf zone (ABA HUSSAIN, 1987). This facies signals the beginning of sea transgression as a result of block or basin subsidence or because of fluctuation in seawater level (AL-BASSAM, 1992). This is followed upward by calci-phos bone ooidal phosphorite facies which also includes ooidals, intraclasts, and corticoid grains and reflects high energy shallow

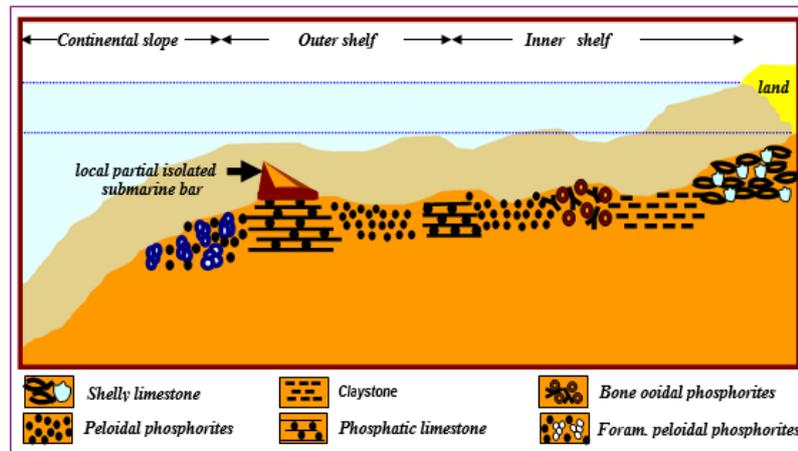


Fig. 8 - The depositional model of phosphorite Akashat Formation (middle Paleocene)

areas exposed to marine currents within the tidal zone. The last facies is followed by phos peloidal phosphorite and calciphos peloidal phosphorite facies alternate with phos limestone facies. The peloidal phosphorite facies indicate the area of intermediate energy of higher depth area which represents the outer shelf region (AL-BASSAM, 1992). The presence of phosphatic limestone facies leads to the thought of a low rate of phosphate deposition derived from up-welling currents as a result of the formation of submarine fences or barriers, or because of local sea regression. The presence of phosphatic limestone facies after each phosphorite facies represents the secondary cycle of seawater regression transgression which begins with phosphorite facies deposition and ends up with deposition of phosphatic limestone facies within the major cycle of transgression throughout middle Paleocene (Fig 8).

CONCLUSION

The biogenesis and diagenesis processes represent two main factors that control the concentration of phosphorous from seawater and the formation of phosphorites in Iraq among other countries of the middle east on the southern Tethys sea coasts; the biogenic processes concentrated phosphorous content as P_2O_5 up to about (5-7) wt%, while the diagenetic processes increasing P_2O_5 to more than 18 wt%, and some time may reach about 34 wt%.

The chemical properties of interfacial waters and seawater affect the chemical composition of francolite mineral, where the interstitial water in the porosity of the upper part of the sea floor mud is enriched on P, Ca and Sr elements resulting from the organic activity of the decay by bacteria, and the organic matter contributes to the adsorption of some elements V and Pb and As and HREE and

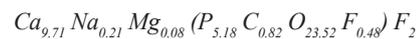
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their fixation on phosphate components. As for the chemical effect of sea water, it is reflected through the enrichment of phosphate components with Na, S, U, Y and LREE elements. Depending on the average mole/formula of the elements in the crystal structure of Akashat francolite, the chemical formula is:



and according to the XRD information it is possible to coin the chemical formula of francolite:



The present study agrees with the phosphate replacement by carbonate (CO_3^{2+}) + fluoride (F^-) because of two reasons: first, the replacement of phosphate tetrahedron by pseudo-tetrahedron of both $CO_3^{2+} + F^-$, and second, the total charge (-3) for ($CO_3^{2+} + F^-$) is similar to the charge of the phosphate root (-3).

The present study supports the mechanism put forward by BATURIN (1982) for P enrichment and phosphorite formation. Therefore, the study adopts general mechanisms "Biogenic-diagenetic phosphorite formation".

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