# Biological processes and apatite formation in sedimentary environments

# Biological processes and apatite formation in sedimentary environments

Krzysztof P. Krajewski[1], Philippe Van Cappellen[2], Jean Trichet[3], Oliver Kuhn[4], Jacques Lucas[5], Agustín Martín-Algarra[6], Liliane Prévôt[5], Vinod C. Tewari[7], Luis Gaspar[8], Robin I. Knight[9] & Michel Lamboy[10]

ABSTRACT

Much of the controversy in the microbial vs. non-microbial phosphorite debate results from a lack of rigor in defining the specific levels at which microbial activity intervenes in phosphogenesis. A clear distinction between the processes that control the sedimentary transformations of particulate phosphorus fractions and the processes that directly participate in the apatite precipitation reaction seems to be necessary in order to reconcile the conflicting views. Microbial processes are the primary driving force behind the transformation of deposited particulate phosphorus into dissolved phosphate, a critical first step in the formation of apatite. The precipitation of apatite itself, however, is widely controlled by kinetic factors. Depending on the initial degree of supersaturation of pore solutions, different mechanisms of the precipitation reaction may prevail in sediments. In most continental margin sediments, low to moderate concentrations of dissolved phosphate may result in a direct nucleation of apatite crystals, leading to a slow formation of dispersed apatite in the sediment column. In phosphogenic sediments, high localized rates of dissolved phosphate generation promote the fast nucleation of a metastable precursor of apatite. This creates a large number of crystallization sites in the sediment, and results in the rapid formation of phosphatic bodies. The transitory fixation and release of phosphate by microbial communities may be responsible, in part, for the elevated concentrations of dissolved pore phosphate observed in close proximity to the water-sediment interface at sites of present-day phosphorite formation (e. g. sediments on the Peru-Chile shelf). Localized pulses of high supersaturation enhance the likelihood of rapid apatite deposition close to the water-sediment interface. Microbial redox processes may further help focusing the rapid precipitation of apatite in the interface environment by telescoping chemical gradients and associated pH shifts in the surface sediment layer. There is no convincing evidence of other important microbial effects being directly involved in the formation of apatite in marine sediments, for instance intra-cellular precipitation of calcium phosphate.

A close association of benthic microbial activity and the formation of apatite can be widely traced in ancient phosphogenic environments. The organic matter of fossil phosphorites preserves a clear molecular signature of the intense degradation of sedimentary organic matter at the seafloor, and points to liberation of phosphorus from organic compounds as a predominant microbial process involved in apatite formation. Ultra-

[1] Polish Academy of Sciences, Institute of Geological Sciences, PL–02–089 Warszawa
[2] Georgia Institute of Technology, School of Earth and Atmospheric Sciences, Atlanta, Georgia 30332, U.S.A.
[3] Université d'Orléans, Laboratoire de la Matière Organique, F–45067 Orléans Cedex 2
[4] ETH-Zentrum, Geologisches Institut, CH–8092 Zürich
[5] Université Louis Pasteur, Centre de Sédimentologie et Géochimie de la Surface, F–67000 Strasbourg
[6] Universidad de Granada, Departamento de Estratigrafía y Paleontología, E–18071 Granada
[7] Wadia Institute of Himalayan Geology, 248001 Dehra Dun, India
[8] R. Academia das Ciencias, Instituto Geologico e Minero, P–1200 Lisboa
[9] University of Oxford, Department of Earth Sciences, OX1 3PR Oxford, United Kingdom
[10] Université de Rouen, Département de Géologie, F–76821 Mont Saint Aignan Cedex

structure analysis of microbial fabrics preserved in phosphorites permits the identification of abundant and diverse benthic microbial communities. Extracellular precipitation of apatite was a common mechanism of microbiota preservation, although no direct cellular control of apatite precipitation can be inferred. The development of localized phosphatic bodies in many ancient phosphorites is likely to reflect the spatial association between the activity of individualized benthic microbial communities and the precipitation of apatite. Stromatolitic phosphorites provide an extreme example of such an association.

ZUSAMMENFASSUNG

Die Kontroverse über die mikrobielle oder nicht-mikrobielle Genese der Phosphorite ergibt sich vor allem aus der Ungenauigkeit der Definition, in welcher Phase mikrobielle Aktivität in die Phosphatgenese eingreift. Um die gegenteiligen Ansichten in Einklang zu bringen, scheint es notwendig zu sein, klar zu unterscheiden zwischen den Prozessen, welche die sedimentäre Umwandlung von nicht gelösten phosphathaltigen Festphasen kontrollieren, und solchen, welche an der direkten Apatitfällung beteiligt sind. Mikrobielle Prozesse sind die hauptsächliche treibende Kraft bei der Umwandlung von sedimentierten, nicht gelösten phosphathaltigen Festphasen in gelöstes Phosphat. Dies ist ein wichtiger erster Schritt der Apatitbildung. Die Fällung von Apatit selber ist dagegen ein Prozess, welcher vor allem durch kinetische Faktoren kontrolliert wird. Je nach dem ursprünglichen Grad der Übersättigung der Porenwässer dominieren verschiedene Mechanismen den Ausfällungsvorgang im Sediment. In den meisten Sedimenten der Kontinentalränder führen tiefe bis mittlere Konzentrationen von gelöstem Phosphat zu direkter Kristallbildung von Apatit. Langsame Bildung von fein verteiltem Apatit im Sediment ist die Folge. In phosphogenen Sedimenten werden hohe Konzentrationen an gelöstem Phosphat eine schnelle Nukleation eines metastabilen Vorläufers von Apatit auslösen. Dies führt zu einer hohen Anzahl von Kristallisationspunkten, was wiederum die schnelle Bildung von phosphatischen Körpern fördert. Die vorübergehende Fällung und Wiederauflösung von Phosphat durch mikrobielle Gemeinschaften könnte teilweise dafür verantwortlich sein, dass in Gebieten heutiger Phosphorit-Produktion (z. B. Sedimente des Schelfs vor Peru) erhöhte Konzentrationen von gelöstem Phosphat im Porenwasser nahe der Wasser/Sediment-Grenze gemessen werden. Lokale Spitzen von hoher Übersättigung verstärken die Wahrscheinlichkeit von schneller Apatitbildung nahe der Wasser/Sediment-Grenze. Mikrobielle Redox-Prozesse mögen ferner dazu beitragen, eine schnelle Fällung von Apatit auf diese Grenzzone zu konzentrieren, indem chemische Gradienten und damit verbundene Verschiebungen des pH in den obersten Schichten teleskopiert werden. Es gibt keine überzeugenden Beweise von andern wichtigen mikrobiellen Effekten, welche direkt an der Bildung von Apatit in marinen Sedimenten beteiligt wären, wie z. B. intrazelluläre Fällung von Calcium-Phosphat. In älteren phosphogenen Sedimenten ist eine enge Beziehung zwischen mikrobieller Aktivität und der Bildung von Apatit weit verbreitet. Das organische Material fossiler Phosphorite zeigt klare molekulare Kennzeichen intensiven Abbaus von sedimentärem organischem Material auf dem Meeresboden. Dies deutet auf eine Freilegung von Phosphor aus organischen Komponenten als wichtigstem mikrobiellem Prozess bei der Apatitbildung hin. Die Untersuchung von Ultrastrukturen mikrobieller Gefüge in Phosphoriten erlaubt die Identifizierung vieler und sehr diverser benthischer mikrobieller Gemeinschaften. Extrazelluläre Fällung von Apatit war ein üblicher Mechanismus der Erhaltung der Mikrobiota, wenn auch keine direkte zelluläre Steuerung der Apatitfällung nachgewiesen werden kann. Die Entwicklung begrenzter phosphatischer Körper in vielen fossilen Phosphoriten scheint den räumlichen Zusammenhang aufzuzeigen zwischen der Aktivität einzelner benthischer mikrobieller Gemeinschaften und der Fällung von Apatit. Stromatolitische Phosphorite sind ein extremes Beispiel einer solchen Vergesellschaftung.

## Introduction

There is much discrepancy in the geological literature concerning the nature of the processes that control the formation of apatite in sedimentary environments. Conflicting hypotheses on inorganic vs. microbial apatite precipitation have been formulated, using various lines of evidence gained from both modern phosphogenic environments and the fossil record. Much of this controversy seems to have arisen from a failure to clearly define the individual processes, microbial or not, that participate in the mineral formation.

In this paper we review the role of biological processes in the formation of authigenic apatite by describing the chemical background and mechanisms of apatite precipitation

in sedimentary marine environments, and by defining the specific levels at which microbial activity may influence, directly or indirectly, the precipitation process. First, we present the biogeochemical processes that determine the generation and distribution of reactive dissolved phosphate necessary for apatite precipitation. Then we discuss the mechanisms and kinetics of the precipitation reactions, and identify specific roles of microbial activity in the initiation of calcium phosphate precipitation and its concentration in sediments. Particular reference is made to a new understanding of marine apatite formation, gained from kinetic and microbial precipitation experiments. Finally, we review available evidence of microbial activity associated with apatite formation in ancient sedimentary phosphorites, and relate this evidence to the processes and controls identified in modern and laboratory systems.

## 1 Biological activity and phosphorus cycling in sediments

### The oceanic phosphorus cycle

The pre-agricultural, steady-state phosphorus cycle at the Earth's surface is illustrated in figure 1. Oceanic phosphorus is divided into particulate organic phosphorus and "reactive" phosphorus. The latter corresponds to the phosphorus which is potentially avaiable for utilization by the biosphere; it consists mainly of dissolved phosphate. Marine life efficiently recycles reactive phosphorus within the ocean system (water column plus surface sediments). Over time, however, small amounts of phosphorus are subtracted from the oceans and incorporated into the sediment repository. The marine sedimentary reservoirs include organically-bound phosphorus that escapes early diagenetic decomposition, phosphate associated with biogenic or authigenic calcium mineral phases (calcium carbonate and carbonate fluorapatite), and phosphate sorbed to ferric (hydr)oxides.

The geochemical phosphorus cycle shown in figure 1 differs from the budget presented by Froelich et al. (1982) by the larger sedimentary masses of phosphorus associated with calcium and iron mineral phases. Recent work on phosphorus speciation in marine sediments by Ruttenberg (Ruttenberg 1990, 1992; Ruttenberg & Berner 1993) has documented apatite precipitation in coastal and shelf sediments that are not associated with major upwelling systems. Although dispersed apatite precipitation in these environments does not lead to the accumulation of economic phosphorite deposits, it represents a significant, and previously unaccounted, sink of reactive oceanic phosphorus. Along similar lines, measurements of iron-bound phosphate in recent marine sediments (Berner et al. 1993) suggest that a significant and, till now, underestimated fraction of reactive phosphorus may be removed from the oceans by burial with ferric oxides in rapidly depositing nearshore sediments. The upward revision of the masses and burial fluxes associated with mineral Ca and Fe bound phosphorus reflects the results from these recent studies on sedimentary phosphorus speciation.

Phosphorus is essential to sustain life. Furthermore, phosphorus, rather than nitrogen, is believed to act as the primary limiting agent of marine biological productivity on geological time scales, because of the ability of the marine biosphere to respond to a long-term nitrate deficiency by fixing more nitrogen from the atmosphere (Redfield 1958; Holland 1978; Broecker & Peng 1982). Consequently, changes in the oceanic cycling of reactive phosphorus have a direct impact on the marine cycles of carbon and other bio-

Reservoirs: mol
Fluxes: x10¹⁰ mol/a
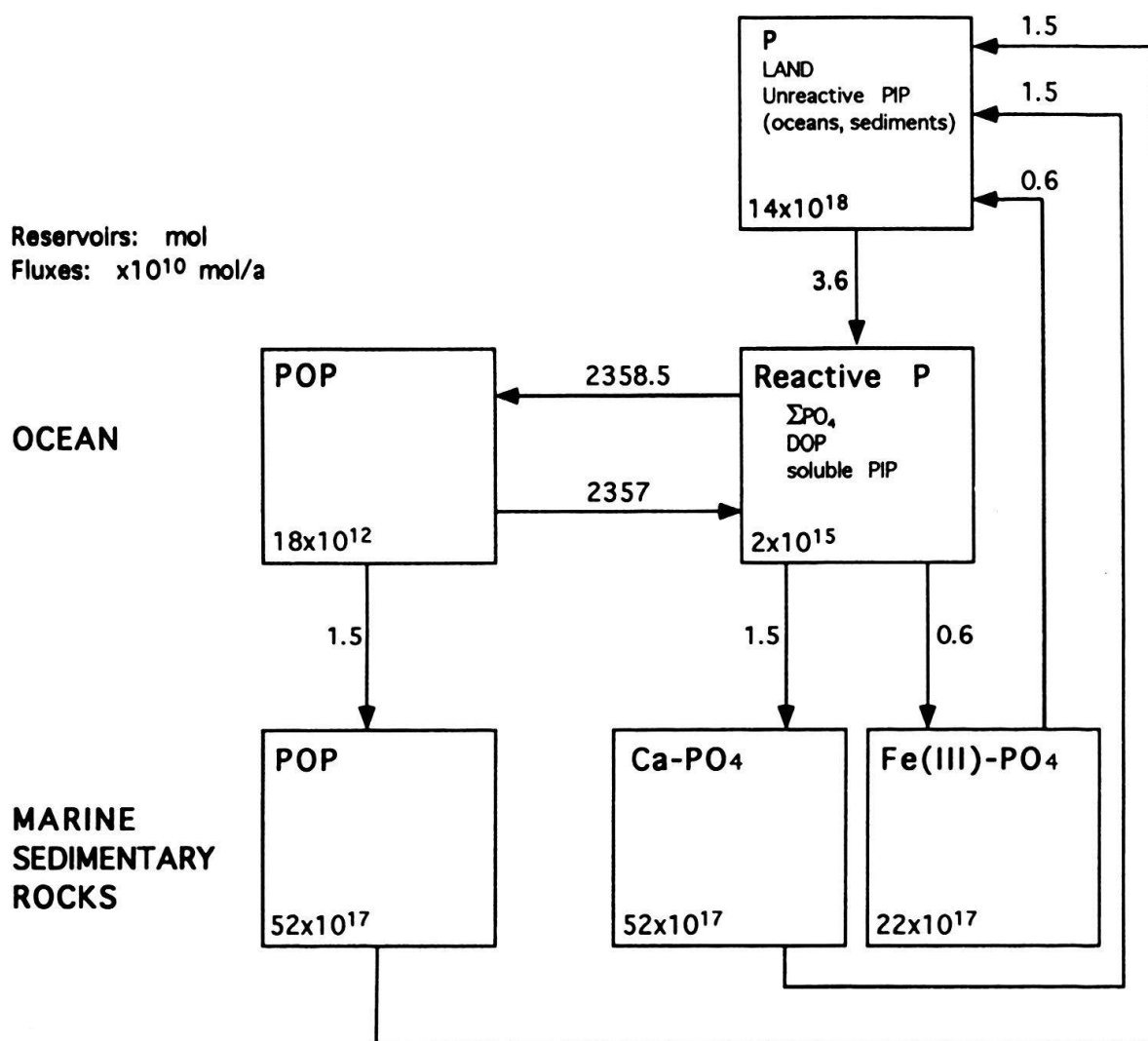


Fig. 1. Steady-state exogenic phosphorus cycle. The figure presents best estimates for the reservoir sizes and fluxes in the phosphorus cycle prior to human perturbation. Note that the sedimentary burial flux of phosphate associated with biogenic and authigenic calcium minerals (mostly calcite and francolite) is thought to be of the same order of magnitude as burial of organic phosphorus. Most of this calcium-bound phosphorus is being deposited in rapidly accumulating sediments along the continental margins. According to the figure, burial of phosphorus in marine sediments represents only 0.15% of the yearly amount of reactive phosphorus fixed into organic matter by net primary production. This illustrates the very efficient recycling of phosphorus in the oceans. Symbols: POP = particulate organic phosphorus; PIP = particulate inorganic phosphorus; DOP = dissolved organic phosphorus. (Van Cappellen & Ingall 1994).

phile elements, as well as on the atmospheric levels of carbon dioxide and oxygen. Thus, the study of the mechanisms that supply and remove phosphorus from the oceans has far-reaching implications for our understanding of the functioning and evolution of the global environment.

## Phosphorus supply to marine sediments

The precipitation of authigenic apatite ultimately depends on the fixation of sea water phosphate into particulate forms, organic or inorganic, and the delivery of the particulate phases to the seafloor. The major processes that incorporate dissolved phosphate in particulate matter are biological synthesis of organic substances, the sorbtion of phosphate to ferric (hydr)oxides and the formation of biominerals.

In the modern ocean, net primary production results in the yearly transformation of about $2.4 \times 10^{15}$ moles of reactive phosphorus into organic particulate matter (Fig. 1). Net primary production settling out of the photic zone is subjected to microbial degradation in the water column. Preferential loss of the nutrient elements P and N from sinking organic detritus has been documented. In the deep-sea, the organic matter arriving at the water-sediment interface may have a carbon to phosphorus ratio as high as $10^3$ (atomic) (Knauer et al. 1979; Suess & Müller 1980). Data on the extent of loss of phosphorus and nitrogen from organic matter during settling are, unfortunately, relatively scarce, especially when dealing with marine environments along the continental margins. Figure 2 shows the C/N and C/P ratios of organic matter in two nearshore sediments. Both ratios increase with depth in the sediment, indicating the preferential remobilization from organic matter of N and P, relative to carbon. Very near the water-sediment interface, however, the ratios are close to those of living marine plankton (C:N:$P_{atomic}$ = 106:16:1), suggesting that little regeneration took place in the water column. This is consistent with the fast sinking rates of marine organic matter (on the order of 100 m per day) and the shal-



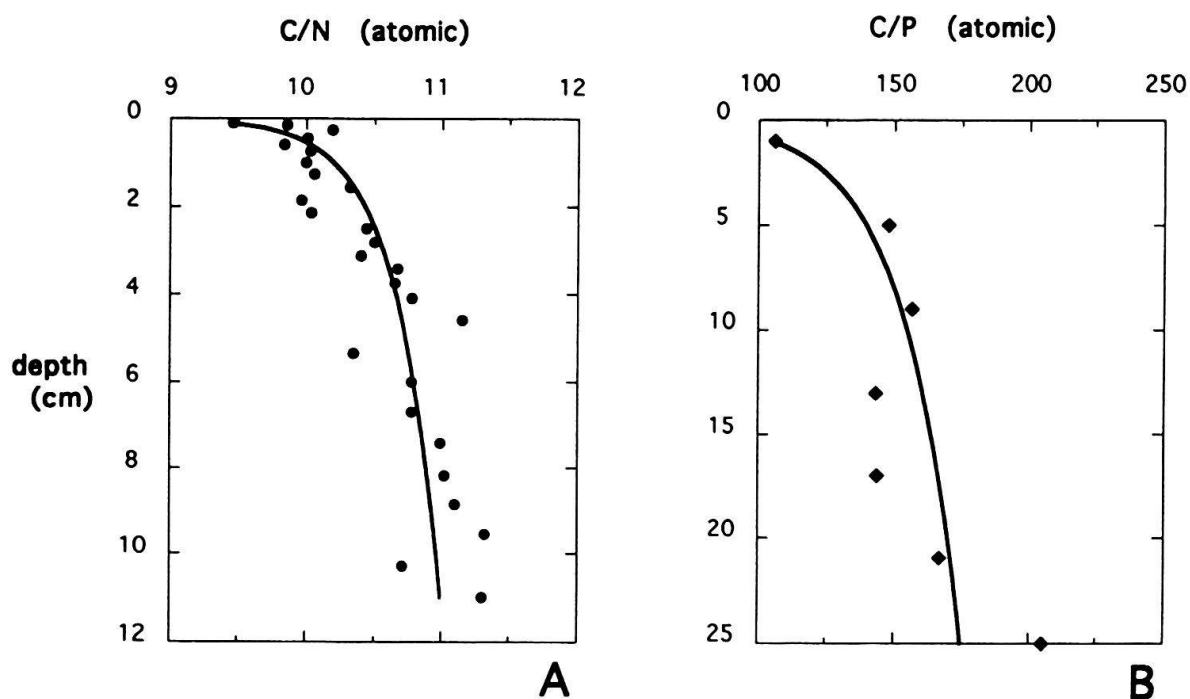Fig. 2. C/N and C/P ratios of organic matter in nearshore marine surface sediments. Both ratios increase with depth in the sediment, indicating the preferential regeneration of the nutrient elements N and P during microbial decomposition of organic matter, relative to carbon. A: sediment from Cape Lookout Bight, North Carolina, USA (data from Martens 1993); B: sediment from the Mississippi Delta, USA (data from Ruttenberg 1990).

low water depths over the continental shelves. The importance of shelves lies in the fact that they account for up to 80–90% of the sedimentary burial of organic matter in the modern ocean, although they only cover about 10% of the seafloor area (Berner 1982).

The world-averaged supply of phosphorus bound to ferric (hydr)oxides at the water-sediment interface is a function of the input of soluble iron to the oceans by rivers, atmospheric dust and hydrothermal vents. It also depends on the state of oxygenation of the water column. Extensive bottom water anoxia, as may have existed during certain periods of Earth's history (e. g. Jenkyns 1980), would cause the reductive dissolution of the ferric (hydr)oxides in the water column, thereby preventing the associated phosphate from reaching the sediments. It has been suggested that with increasing water column anoxia phosphorus removal from the oceans is increasingly diverted from phosphorus burial with organic matter and ferric (hydr)oxides to burial of calcium-associated phosphate (Van Cappellen & Ingall 1994; see also Jarvis et al. 1994).

Biological activity also fixes reactive phosphorus in biogenic mineral phases, i. e. calcium carbonate and hydroxyapatite (Berner et al. 1993). In certain marine environments, skeletal debris may represent a major supply of phosphorus to the sediments (Suess 1981). Biologically produced hydroxyapatites forming the mineral compounds of bones and teeth are soluble in seawater and undergo rapid dissolution after death of the organisms (Nriagu 1983). However, many uncertainties remain concerning their importance in the benthic phosphorus cycle.

The amount of phosphorus, both organic and mineral, which ultimately is buried in marine sediments reflects an interplay between the supply of particulate phosphorus forms to the sediment surface and their regeneration to the oceanic reservoir. The organic phosphorus is buried mainly in the form of phosphate esters and phosphonate compounds, which remain in a refractory fraction after biological utilization of organic matter (Corbridge 1985; Ingall et al. 1990; Berner et al. 1993). This phosphorus fraction is buried at low but relatively uniform rates throughout the oceans, regardless of the actual phosphorus budget of the depositional environment (Froelich et al. 1982). The accumulation rates of mineral phosphorus show much wider variations. They depend on the rate of supply of particulate phosphorus to the seafloor, and on the overall sedimentation rate. Figure 3 shows a plot of sedimentation rate and total phosphorus accumulation rate calculated for a spectrum of marine sediments. At a given sedimentation rate, the phosphorus accumulation rates of P-rich sediments (P > 1%) are higher by a factor of $10^2$–$10^3$ in comparison to P-poor sediments (P < 1%). In general, this difference coincides with a difference in the supply of particulate phosphorus to sediments in low vs. high biological productivity regions (Baturin 1982; Romankevich 1984). Despite the good correlation between the phosphorus accumulation and bulk sedimentation rate, no clear correlation is observed between the actual accumulation rate and the concentration of phosphorus in sediments (Fig. 4). Thus, large amounts of inorganic phosphorus may be buried in sediments that do not display anomalously high concentrations of mineral P. It also means that the benthic processes, physical and biological, which promote high concentrations of authigenic calcium phosphate mineral operate over a wide range of bulk sediment and phosphorus accumulation rates. Physical concentration processes are beyond the scope of this paper. The involvement of microbiological processes in the benthic immobilization and concentration of phosphorus is discussed further on in this paper.
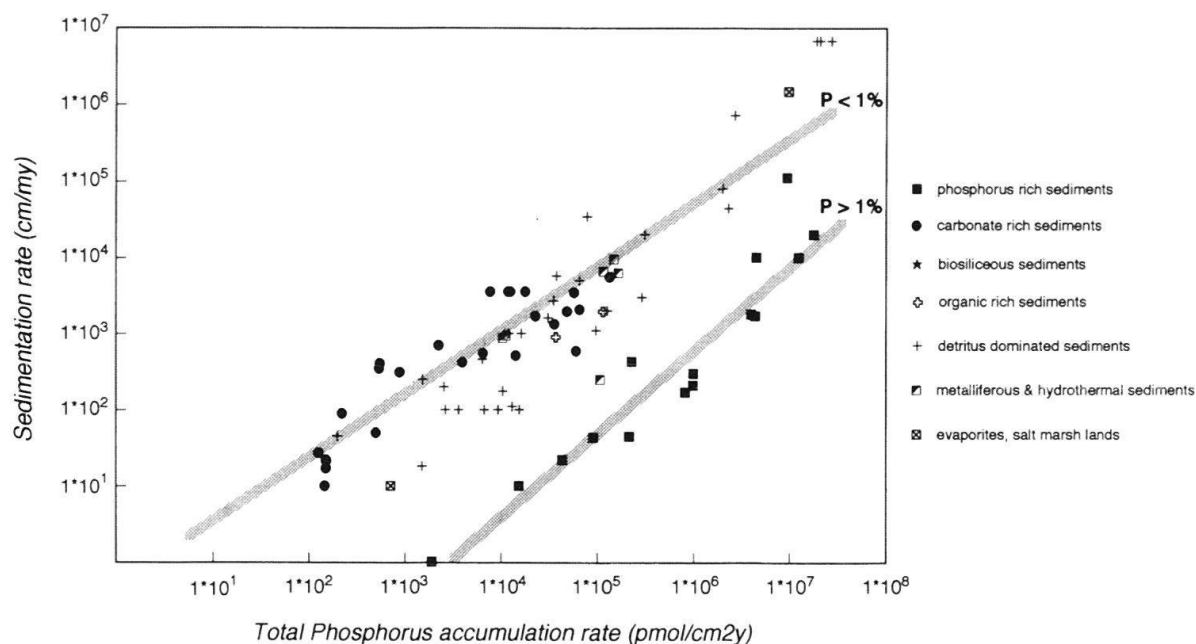
Fig. 3. A plot of the phosphorus accumulation rates and net sedimentation rates calculated for a spectrum of marine phosphorus-rich (P > 1%) and phosphorus-poor (P < 1%) sediments. Most data used for the calculations were collected from DSDP and ODP Legs (see references below). The time scale of Harland et al. (1989) was used to calculate net sedimentation rates. Dry bulk densities of sediments were calculated from wet bulk densities and water contents, with average values applied in cases where appropriate physical data were missing. P-accumulation rates were calculated by using the equation formulated by Filipelli & Delaney (1993a). The phosphorus contents and dry bulk densities of sediments were averaged from sediment column intervals showing maximum vertical uniformity of sedimentation rates. Calculation and data compilation by O. Kuhn. References: Al Bassam (1989); Arthur et al. (1985); Atfeh (1989); Baker & Allen (1990); Berker (1989); Boström & Backman (1990); Boström et al. (1976); Brumsack (1991); Chamley & Debrabant (1984); Crowley et al. (1990); Cunningham & Kroopnick (1981); Dean et al. (1984); Emelianov & Timonis (1983); Emelianov et al. (1978); Filipelli & Delaney (1993b); Haldimann (1977); Heath et al. (1986a; 1986b); Jarrard & Lyle (1991); Jarvis (1985); Kurnosov & Chudaev (1983); Kurnosov et al. (1983); Leggett (1982); Lisitzin et al. (1971); Lyle (1983); Migidisov et al. (1983); Minai et al. (1986); Monciardini (1989); Murray & Leinen (1993); NTB 84–34 (1984); Office Cerifien (1989); Pickering & Stow (1986); Robaszinsky (1989); Schrader et al. (1980); Sheldon (1989); Schimmield & Mowbray (1991); Varentsov (1981; 1983); Varentsov et al. (1981a; 1981b); Zwolsman et al. (1993).
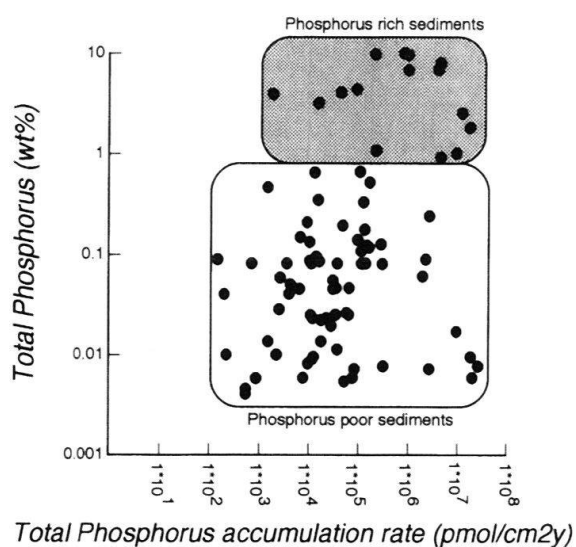


Fig. 4. A plot of the calculated phosphorus accumulation rates and the phosphorus contents of a spectrum of marine phosphorus-rich (P > 1%) and phosphorus-poor (P < 1%) sediments. The figure shows no clear correlation between the phosphorus accumulation rate of marine sediments and burial concentrations of phosphorus for either of the two sediment types. For references see figure 3.

*Benthic phosphorus cycling*

The most intense biogeochemical activity in sediments is concentrated within the surface layer. The water-sediment interface separates the water column, with its large scale fluid motion and turbulent mixing, from the sediment where molecular diffusion typically dominates solute transport. For particulate matter, the transfer across the water-sediment interface represents a transition from a relatively rapid sinking regime to a much slower sediment accumulation rate. Thus, compared to the water column, surface sediments may be viewed as semi-confined environments characterized by long residence times of the particulate matter. These conditions favour the extensive biogeochemical processing of the deposited materials, and the establishment of steep compositional pore water gradients, examples of which are given in figure 5.

Microbial activity is involved, directly or indirectly, in most of the chemical changes affecting phosphorus in surface sediments. Figure 6 illustrates some of the transformations that phosphorus undergoes during early diagenesis. Dissolved pore water phosphate plays a central role as the intermediate species between the various particulate phosphorus reservoirs. The retention of phosphorus in a sediment, e. g. under the form of authigenic apatite, depends on the efficiency with which a sediment can counteract the diffusive loss of dissolved phosphate to the overlying water column.

The production of dissolved pore water phosphate by the degradation of organic matter is carried out by microbial heterotrophs inhabiting the sediment (e. g. Van Cappellen et al. 1993). Microbial activity may also be involved in the acceleration of the dissolution of phosphatic skeletal remains in sediments (Smith et al. 1977). In organic-rich depositional environments overlain by oxygenated bottom waters, aerobic respiration results in the depletion of pore water oxygen at some depth below the water-sediment interface. The reductive dissolution of ferric (hydr)oxides at the oxic-anoxic interface may be a substantial source of dissolved pore water phosphate (Van Cappellen & Berner 1988). Recent studies have confirmed that sedimentary microorganisms can directly couple the reduction of iron oxides to the oxidation of organic carbon (e. g. Lovley & Phillips 1988). In addition to dissimilatory iron reduction, bacterial activity may directly promote iron oxide reduction via the production of reactive reductants, such as dissolved sulphide (Burdige & Nelson 1986).

The retention in the sediment of remobilized phosphate is a function of the sediment accumulation rate, the intensity at which the sediment is irrigated and mixed, the rate of microbial phosphate uptake, and the precipitation kinetics of calcium phosphate minerals. The latter is strongly dependent on the degree of supersaturation of sediment pore waters (see section 2). We speculate that benthic microorganisms, e. g. microbial mat communities, can exert a strong influence on the pore water levels of dissolved phosphate through their ability for active uptake and release of phosphorus from the aqueous medium.

Exchange of phosphate between bacteria and pore waters is modulated by the redox conditions of the interstitial environment (Gächter et al. 1988; Carlton & Wetzel 1988; Ingall et al. 1993). Under aerobic conditions, and when excess dissolved phosphate is available, microorganisms accumulate and store phosphorus as the end result of oxidative phosphorylation (Toerien et al. 1990). Upon depletion of oxygen, the bacterially stored phosphorus is utilized as an energy source and eventually released as dissolved
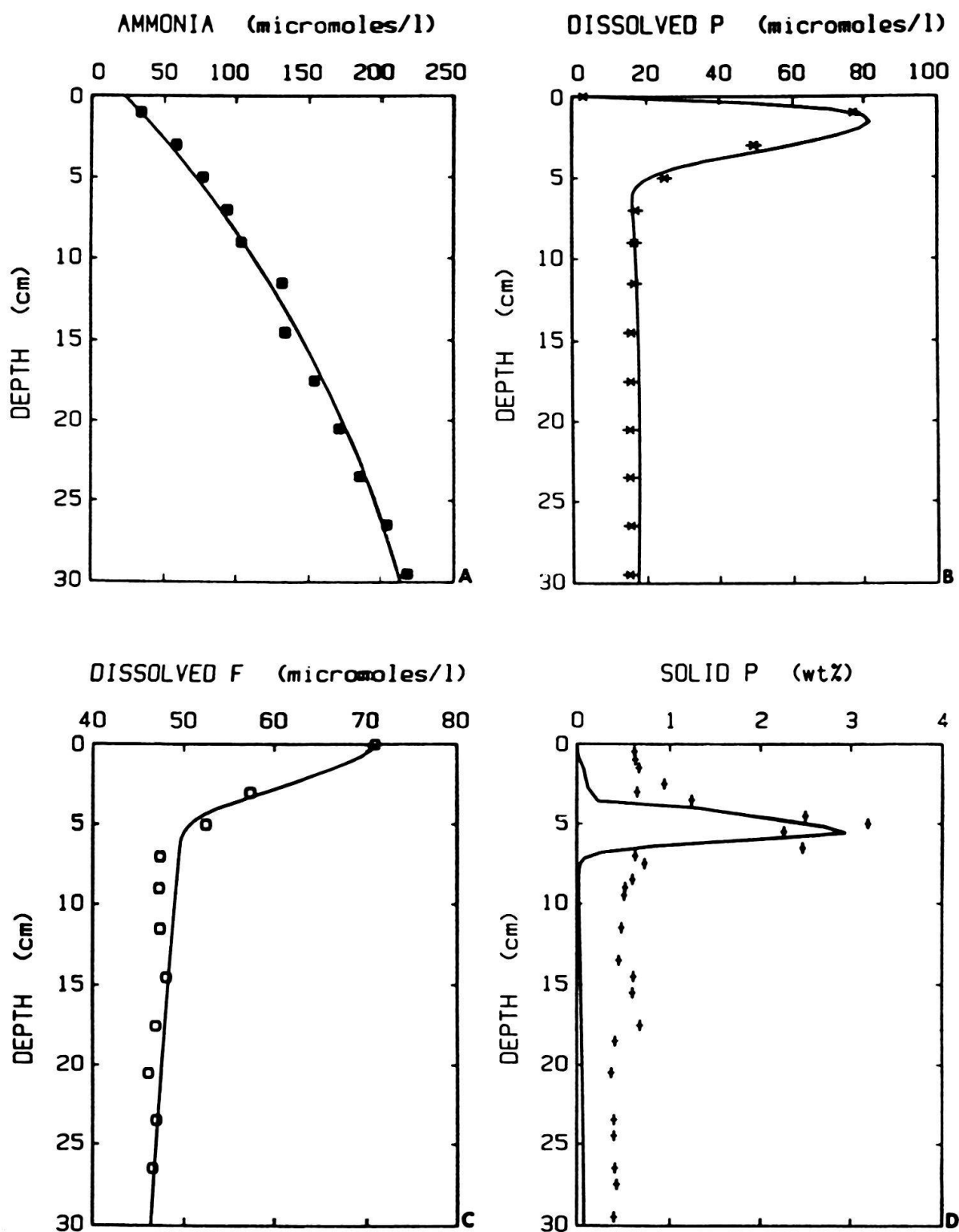
Fig. 5. Pore water and solid sediment data from a Mexican Pacific continental margin sediment (Jahnke et al. 1983). This site is characterized by a high surface water biological production. A layer of authigenic apatite is presently forming in the sediment. The position of the layer, at approximately 5 cm depth below the water-sediment interface, is indicated by the maximum in solid phosphorus concentration and the inflections in the pore water phosphate and fluoride profiles. The solid lines through the data are the calculated results of a transport-reaction model which accounts for apatite precipitation in the sediment (see Van Cappellen & Berner 1988).

## REACTIVE PHOSPHORUS

Boundary conditions
+ deposition fluxes
+ oxygen concentration
+ bacterial mats

Organic P
deposited

Organic P
benthic biomass

Biogenic
mineral P

Dissolved P
PO4, DOP

Authigenic
mineral P

Fe(III)oxide-P

Bacterial
Stored P

Exchangeable
Phosphorus

Driving parameters

+ sedimentation rate
+ intensity of bioturbation
+ flux and reactivity organic matter
+ redox conditions bottom water

Fig. 6. Early diagenetic transformations of phosphorus. As a result of a variety of processes, most of which are microbially mediated, phosphorus is remobilized from deposited organic matter, biogenic mineral debris and ferric (hydr)oxides. The dissolved phosphorus that is produced will diffuse out of the sediment, unless it is fixed in the tissues o benthic organisms, precipitated as a phosphate mineral, coprecipitated with ferric (hydr)oxides, or adsorbed onto detrital particles. It is proposed here that the ability of benthic microbiota to actively store and release pore water phosphate, in response to changes in redox conditions, may be intimately involved in the initiation of phosphorite formation (see text).

phosphate to the surrounding waters. This redox-dependent physiological mechanism may provide a means to trap and concentra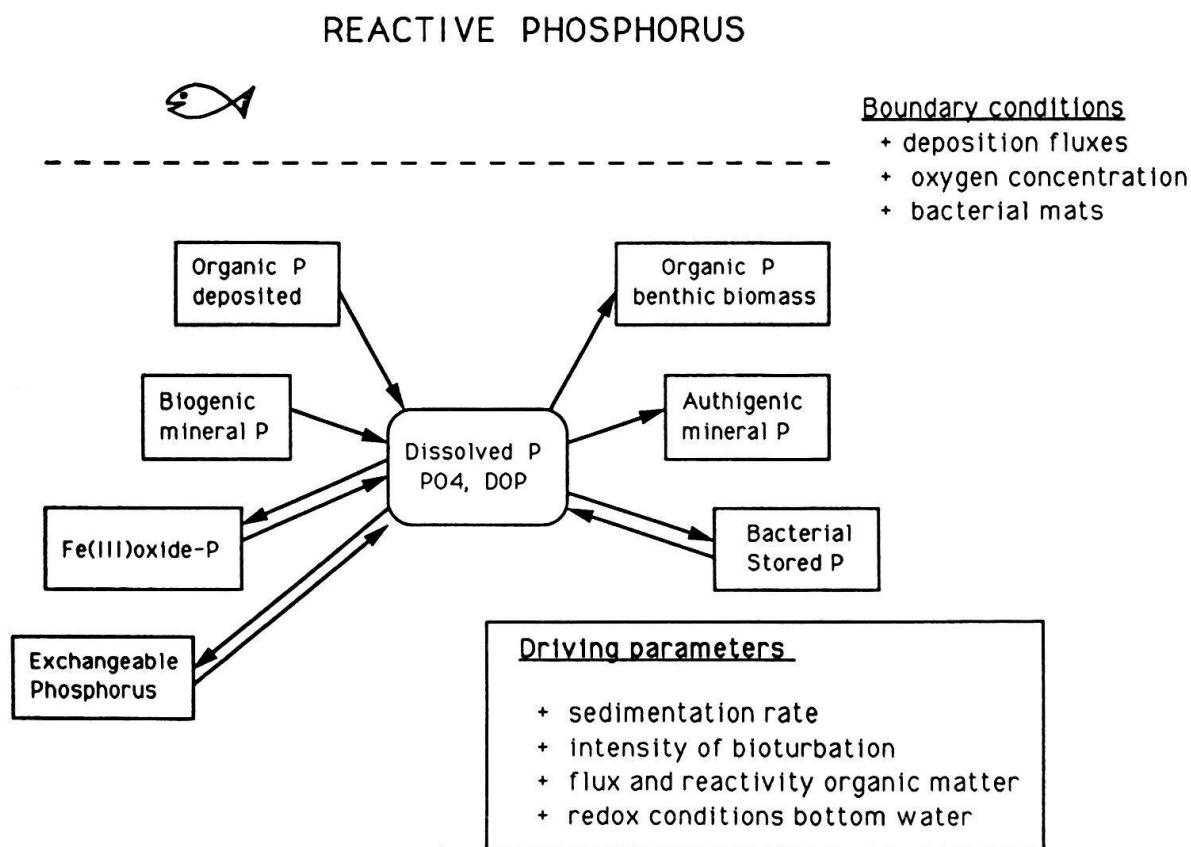te dissolved phosphate, produced over the entire depth of a sediment, into the aerobic surface layer. Subsequent burial of the surface layer and its bacterial population and/or fluctuations of the oxic-anoxic boundary may cause pulses of dissolved phosphate release close to the water-sediment interface, creating the necessary conditions for the rapid nucleation of a calcium phosphate mineral. Interestingly, redox cycling of phosphate regulated by bacterial uptake and release or by abiotic precipitation and dissolution of ferric (hydr)oxides both result in the immobilization of dissolved phosphate under oxic conditions and its release under anoxic conditions.

The proposed "microbial" redox mechanism for initiating authigenic apatite formation is speculative but, we believe, worthy of further investigation. In particular, the deployment of benthic chambers in areas of modern phosphatic sediment accumulation appears as a promising approach to test the role of a microbially-mediated redox cycling of sediment phosphate. These studies could be designed after the benthic chamber experiments of Gächter et al. (1988) in lake environments. In these experiments, the water

masses enclosed by the chambers were allowed to cycle through oxic and anoxic periods. Monitoring of oxygen, soluble reactive phosphorus and dissolved iron in the chambers showed that the uptake and release of dissolved phosphorus was partly the result of physiological response of the sedimentary microorganisms.

The scenario described above implies that rapid nucleation of calcium phosphates should take place preferentially in a surface sediment overlain by oxygen containing bottom waters and inhabited by a dense microbial community (see sections 2 and 3). Extensive irrigation, bioturbation and the presence of a large population of microbial grazers are probably unfavourable for the development of a stable microbial community at the water-sediment interface. This means that the microbially-mediated redox pump would be most effective in promoting phosphate precipitation under dysaerobic rather than fully aerobic bottom waters. This is consistent with the observation that modern phosphorites typically form where oxygen minimum zones impinge on the seafloor. Continued research, however, is necessary to fully understand the effects of benthic microbial activity on the early diagenetic cycling of phosphorus and its role in phosphorite formation.

## 2 Apatite precipitation in sediments

*Kinetic regimes of sedimentary apatite formation*

This section is based primarily on the results of the work by Van Cappellen (1991), who investigated the precipitation of fluorapatite (FAP) under simulated marine conditions (see also Van Cappellen & Berner 1991). This work identified different pathways of authigenic apatite formation. It was shown that FAP may form via the initial nucleation of a metastable calcium phosphate precursor phase. The nature of the initial precursor and its further transformation pathway depends on the initial degree of supersaturation of the aqueous solution. The results of the study, however, also showed that at sufficiently low degrees of supersaturation FAP may nucleate directly from solution, without the initial formation of a chemically distinct precursor.

Whether or not fluorapatite precipitates via the formation of precursors has a profound effect on the overall kinetics of the precipitation reaction. The direct nucleation of FAP from solution is a slow process and, hence, it is not very effective at producing reactive mineral surface area that can be used for crystal growth. As a result, when precipitation is initiated by direct nucleation of apatite, the onset of precipitation is characterized by long induction periods and the resulting overall rates of apatite precipitation are low (note: the overall rate of precipitation refers to the mass of mineral formed per unit volume solution or sediment). In the experimental work mentioned above, metastable solutions supersaturated with respect to FAP could be maintained for periods exceeding several months without any precipitation being detectable.

From a certain degree of supersaturation on, the precipitation reaction is initiated by the nucleation of a more soluble precursor phase rather than by direct nucleation of apatite. The explanation of this behavior lies in the kinetics of the precipitation process. The system preferentially forms the phase with the fastest precipitation rate under the prevailing conditions. The nucleation of a less stable precursor is kinetically favoured over that of FAP, because the precursor has a lower solid-solution interfacial energy. Two distinct precursors were identified: an octacalcium phosphate-like precursor ($OCP_p$) and

amorphous calcium phosphate (ACP). In the presence of dissolved magnesium, the amorphous precursor incorporates significant amounts of $Mg^{2+}$ ions and the solid phase is more appropriately referred to as amorphous calcium magnesium phosphate (ACMP). Interestingly, all the precursors observed in the experimental study contained little fluorine although the seawater medium had a fairly high fluoride concentration (100 μM). Thus, the transformation of precursors into apatite involves the uptake of fluoride.

The initial solution composition determines the solid calcium phosphate phase that precipitates first and, hence, the reaction pathway by which apatite is formed. This is illustrated in figure 7, for the formation of fluorapatite in magnesium-free modified seawater. The figure shows the induction times for the spontaneous precipitation of FAP and the precursors $OCP_p$ and ACP. The phase nucleating initially from solution is that with the shortest induction period, for the given initial degree of supersaturation. The compositional domains are essentially delimited by the solubilities of the solid phases.

Relative to the direct nucleation of stable FAP, the nucleation of a precursor is a fast process. As a consequence, it rapidly creates mineral surface area that can be used for precipitation. The appearance of a more stable mineral requires that either the precursor serves as an epitaxial template for growth of the more stable phase or converts into the latter. As a general rule, the formation of apatite via a pathway including precursors is expected to be kinetically more effective than via direct nucleation.

The levels of supersaturation required to initiate the formation of ACP, ACMP or $OCP_p$ ($\Sigma PO_4$ = 400–600 μM) are not commonly encountered in natural marine sediments. In coastal areas of rapidly accumulating, organic-rich sediments, for example the Santa Barbara Basin (Sholkovitz 1973) and Long Island Sound (Goldhaber et al. 1977), the regeneration of organically bound phosphorus takes place over depths of one to sev-
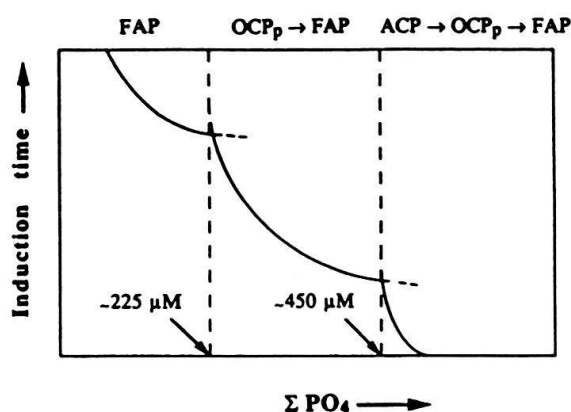


Fig. 7. Induction time for calcium phosphate precipitation as a function of supersaturation. The induction period is the amount of time between the moment supersaturation is created and the onset of precipitation. Time is in arbitrary units, supersaturation is expressed as the total dissolved phosphate concentration in Mg-free artificial seawater (pH = 8, t = 25°C). At any given degree of supersaturation, precipitation is initiated by the phase with the fastest nucleation rate, i. e. the shortest induction period. The corresponding reaction pathways are indicated. The compositional domains are bound by the solubilities of the precursor phases (OCP and ACP). At phosphate concentrations lower than approximately 225 μm$^P$, apatite formation is initiated by direct nucleation of apatite crystals. This is an extremely slow process, because of the high interfacial free energy between apatite and aqueous solutions. Rapid phosphorite formation as observed in a number of modern sediments underlying areas of coastal upwelling can be explained by the fast nucleation of a metastable precursor with a lower interfacial free energy (see also Fig. 8).

eral meters (Van Cappellen & Berner 1988). The interstitial phosphate concentrations typically increase monotonically with depth, and may attain levels of 100–300 μM. The pore waters become strongly supersaturated with respect to fluorapatite, and there is evidence for authigenic apatite formation at some nearshore sites (Ruttenberg & Berner 1993). However, the rate at which dissolved phosphate is removed as authigenic apatite is very slow and, typically, does not succeed in reversing the downward increasing trend of pore water phosphate, as observed in the case of more rapid apatite precipitation (Van Cappellen & Berner 1988). It is the inefficient production of reactive surface area by direct nucleation of apatite that allows supersaturation to build up and be maintained in these sediments.

The direct nucleation of apatite in a layer of sediment that is progressively buried will produce a slowly increasing number of apatite crystals. At some depth, nucleation and growth of apatite probably stop because of the rising level of carbonate alkalinity accompanying decomposition of organic matter (Jahnke 1984; Glenn et al. 1988). Hence, under steady state conditions, the authigenic apatite content of the sediment should increase progressively with depth and level off at some constant value. Field evidence of this type of *dispersed apatite precipitation* in coastal sediments deposited outside strong upwelling areas has been presented by Ruttenberg & Berner (1993).

One potential environment where the formation of apatite may be initiated by the nucleation of a less stable precursor is the topmost sediment on continental shelves under areas of intense coastal upwelling, such as the Peru-Chile shelf (see also Jarvis et al. 1994). The upper few centimetres of sediment in these settings are often characterized by a marked maximum in the dissolved pore water phosphate concentration (Jahnke et al. 1983; Froelich et al. 1988; see Fig. 5). The mechanism producing the interfacial maximum in pore water phosphate is not well understood. Its magnitude cannot be explained simply by the decomposition of sedimentary organic matter (Froelich et al. 1988; Van Cappellen & Berner 1988). As suggested in section 1, the pore water phosphate maximum may be related to the redox-sensitive uptake and release of phosphorus by microbial communities proliferating in the top sediment. The low oxygen conditions in the bottom waters restrict operation of the bacterial redox-pump to a very narrow layer underneath the water-sediment interface, below which the sediment is completely anoxic. The absence of abundant oxygen also limits the disturbance of the interfacial environment by macrofaunal activity.

The pore water phosphate concentrations that have been measured in surficial sediments from upwelling areas are below the solubility of the apatite precursors identified in the present study. Nevertheless, there are indications that conditions of supersaturation with respect to the apatite precursor(s) are periodically produced in the topmost sediment and result in a fast precipitation of the precursor.

Modern phosphatic material from sediments deposited beneath coastal upwelling currents occurs mainly as nodules, layers and pellets, i. e. precipitation of sedimentary apatite seems to be confined spatially (Veeh et al. 1974; Price & Calvert 1978; Jahnke et al. 1983; Kim & Burnett 1986; Glenn & Arthur 1988, Lamboy 1990b). Once initiated, the precipitation of apatite in a phosphatic body takes place very rapidly. For example, Jahnke et al. (1983) and Van Cappellen & Berner (1988) have shown that precipitation of apatite, in a phosphorite layer presently forming at the site along the western Mexican continental margin, causes an enrichment of several weight % authigenic phosphorus over a period of only a few hundreds of years.

The formation of a phosphatic body is apparently initiated by a rapid nucleation event that produces locally a very high concentration of nuclei. Further phosphate precipitation is then directed towards the locus of initial nucleation, with pore water diffusion supplying the dissolved ions. The presence of many growth nuclei in a small volume of sediment explains the rapid accumulation of authigenic phosphorus under the form of nodules, pellets and layers. High concentrations of growth sites in phosphatic bodies were recently confirmed by scanning electron microscopy study of Lamboy (1990b) on a phosphatic crust recovered off the coast of Peru. Lamboy estimates that the number of individual apatite particles in the crust exceeds $10^9$ cm$^{-3}$. The particles in the younger part of the crust are rod-shaped with rounded ends and have a subcircular section. The particles are typically micron-sized. However, in the older part of the crust the particles develop a prismatic habit with a hexagonal section, characteristic of apatite. The observations are consistent with the rapid initial nucleation of precursor particles, followed by the appearance of apatite. Growth and aging leads to a progressive improvement of the crystallinity of apatite (Kim & Burnett 1986; Van Cappellen & Berner 1991).

Pore water chemical data collected by Froelich et al. (1988) in the upper 20–40 cm of Peru shelf sediments lend further support to the initiation of apatite formation by a precursor similar to those identified in the experimental study of Van Cappellen. These authors found that for a number of sites the uptake of dissolved phosphate is uncoupled from the uptake of fluoride, with the former preceding the latter. This is exactly what one would expect if the formation of apatite is initiated by the precipitation of a precursor that is poor in fluoride (e. g. ACMP or OCP$_p$), followed by the transformation of the precursor in carbonate fluorapatite.

If a precursor with a low interfacial tension nucleates from the pore waters, we do not expect the precipitate to demonstrate a strong preference for a particular solid substratum, as nucleation may be partially or predominantly homogeneous. The diversity (and sometimes absence) of solid surfaces around which pellets, grains and nodules of phosphate are found to form (Slansky 1986; Glenn et al. 1988) seems to corroborate a lack of substrate specificity.

Once initiated, the rapid precipitation of apatite depletes the surrounding pore waters of dissolved phosphate (and fluoride). This brings down the pore water supersaturation towards apatite solubility (Van Cappellen & Berner 1988) and effectively halts nucleation. Thus, on an early diagenetic time scale *the nucleation of a precursor is a short-lived phenomenon.* Rapid depletion of pore water supersaturation by growth of apatite explains why the measured pore water phosphate levels in sediments from upwelling areas are usually found to be undersaturated with respect to the precursors.

Figure 8 shows schematically the possible succession of events as a phosphatic body (e. g. a layer or pelletal bed) that started to form close to the water-sediment interface is progressively being buried along with the accompanying sediment, under conditions of continuous sedimentation. As the phosphatic body is buried deeper and deeper, supersaturation is allowed to build up again close to the water-sediment interface. The reason for this is simply that the sink of phosphate (i. e. apatite precipitation in the phosphatic body) is moving away from the top sediment where the most intense production of dissolved phosphate occurs. This has been shown by a series of computer simulations of the non-steady state effect of the burial of an apatite layer on pore water phosphate and fluoride profiles (Van Cappellen & Berner 1988). Actual pore water profiles showing a strik-
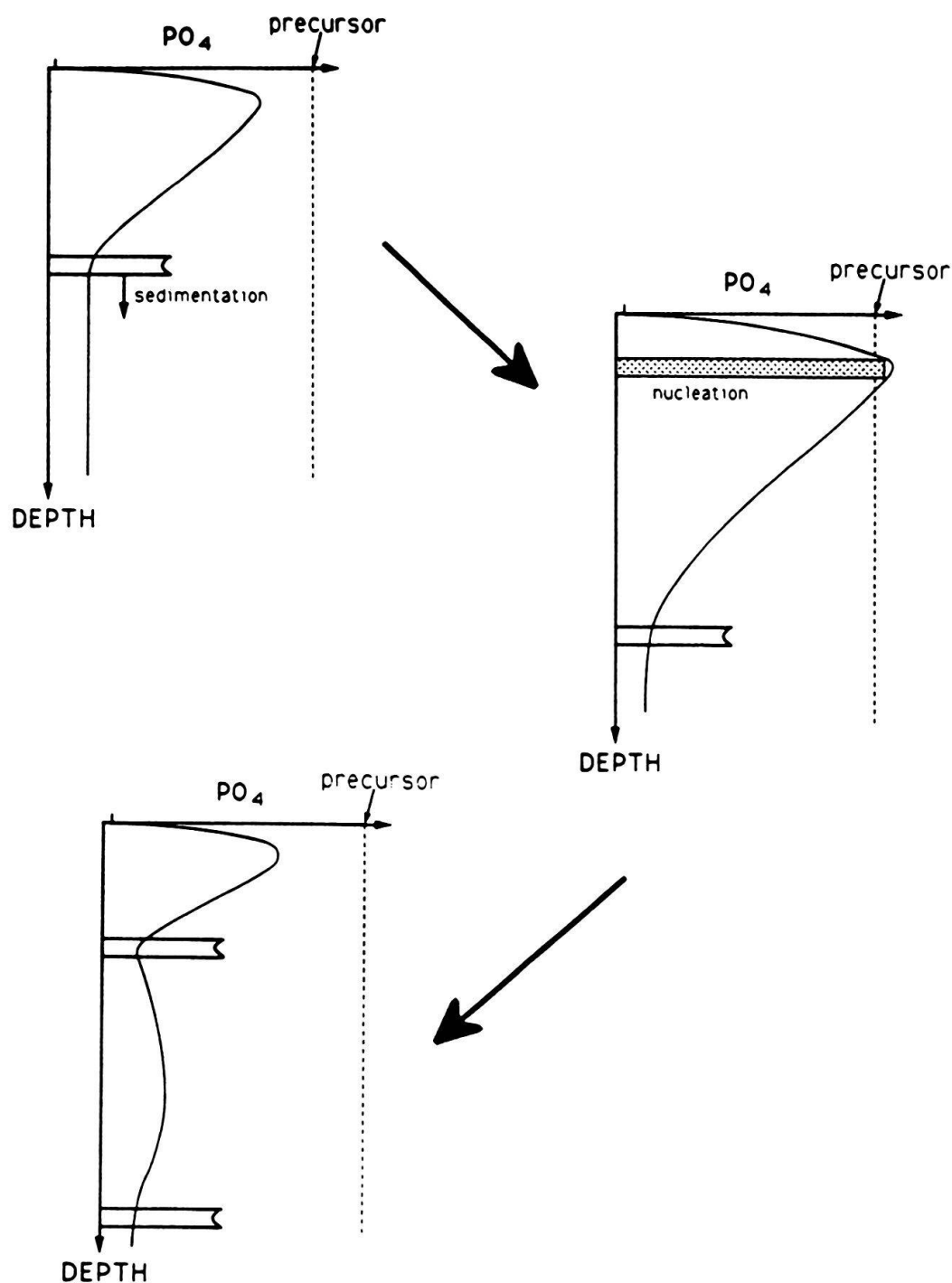
Fig. 8. Schematic representation of the repetitive formation of phosphatic layers during continuous sediment accumulation. The figures are inspired from computer simulations in Van Cappellen & Berner (1988). Shown on the figure are successive dissolved pore water phosphate profiles plotted as a function of depth below the water-sediment interface, and the corresponding positions of the phosphatic layers. It is assumed that the early diagenetic production of pore water dissolved phosphate does not vary significantly over time. Thus, the changing pore water phosphate profiles reflect the burial of the phosphatic layers that act as sinks of dissolved phosphate. The broken line represents the solubility of a precursor. For simplicity the solubility of the precursor is depicted as a constant dissolved phosphate level, although the saturation phosphate concentration may conceivably vary with depth as a result of changing pore water chemistry (e. g. changes in the carbonate alkalinity). The middle profile illustrates the nucleation event initiating the formation of a new layer, when the dissolved phosphate level in the top sediments exceeds the solubility of the precursor.

ing ressemblance to the calculated ones have been presented by Jahnke et al. (1983). Thus, it is conceivable that when the first layer is buried deeply enough, conditions for a new nucleation of a precursor will exist again in the topmost sediment, and the formation of a new layer is initiated (Fig. 8). Schuffert (1988) and R. A. Jahnke (personal communication) have observed a succession of apatitic layers in a sediment core from an upwelling site on the Mexican Pacific continental margin, which could be explained by the episodic nucleation scenario presented here.

Multiple phosphorite layers are an example of pattern formation driven by non-linear precipitation kinetics. The non-linearity of the precipitation process derives primarily from the high degree of supersaturation required to induce the fast nucleation of a precursor phase. The coupling of the non-linear precipitation kinetics to sediment advection allows a repetition in time and space of the formation of apatite layers. However, only in the case of uninterrupted sediment deposition should one expect the formation of a more or less regular succession of layers as depicted in figure 8.

When important reworking and winnowing occur, the sediment will display a more complicated record. This is probably the case for many of the modern sediments retrieved from the Peru-Chile continental shelf (Reimers & Suess 1983; Glenn & Arthur 1988), in which phosphatic crusts and nodules show evidence for more than one episode of growth, suggesting successive periods of sediment accumulation and erosion.

Ancient sedimentary phosphorite accumulations also frequently show evidence of non-steady state sediment accumulation, with successive cycles of erosion and reburial. Nevertheless, even in non-steady state depositional environments, phosphorite formation seems to be initiated by episodic events that allow rapid, localized nucleation. For example, Föllmi & Garrison (1991) have presented detailed sedimentological evidence suggesting that the formation of phosphatic laminae in the Miocene Monterey Formation of California is triggered by episodic sediment relocations that suddenly bury prolific benthic communities, including microbial mats. By combining knowledge about early diagenetic processes with an understanding of the reaction mechanisms and kinetics of apatite precipitation, it becomes possible to provide a logical framework in which sedimentological observations such as those presented by Föllmi & Garrison can be interpreted. Thus, the rapid burial of a benthic community by a gravity flow will expose a highly concentrated accumulation of reactive organic matter to microbial degradation. The ensuing intense release of dissolved phosphate can then locally create the required level of supersaturation to rapidly nucleate a metastable precursor, and hence initiate the formation of a new phosphatic lamina.

*Microorganisms and apatite formation*

Sedimentary microorganisms are an integral part of the formation of authigenic apatite. They drive the oxidation of organic matter and the reduction of ferric (hydr)oxides, and they accelerate the dissolution of mineral fish debris. In other words, they regulate the rate at which dissolved phosphate is released from the reactive sedimentary phosphorus reservoirs to the pore waters (Fig. 6). Benthic microorganisms, however, may play other roles in the formation of authigenic apatite. The ability of microbiota to transitorily accumulate pore water dissolved phosphate (see section 1), and to modify the chemistry of the pore environment affects the localization of apatite precipitation in sediments. Micro-

organisms can increase rates of chemical reactions leading to the apatite precipitation, which would take a very long time to reach equilibrium under abiotic conditions. They may actively alter the concentrations and the activities of dissolved ionic species taking part in the precipitation reaction, thereby creating chemical conditions for a rapid and localized development of the mineral phase. Also, the abundance of microorganisms in the precipitation environment may lead to the apparent concentration of authigenic apatite on biological substrata. The above microbial effects are expected to be especially pronounced in situations where the surface layers of phosphogenic sediments are dominated by dense microbial communities, in particular microbial mats.

At sites of contemporaneous phosphate formation, microbial mats dominated by colourless filamentous sulphur bacteria are often found to occupy the water-sediment interface (Gallardo 1977; Soutar & Crill 1977; Rosenberg et al. 1983; Henrichs & Farrington 1984). The role of these mats in phosphogenic processes is not well understood, although we suggest that it could be related to the ability of colourless sulphur bacteria to actively accumulate dissolved phosphate generated in the sediment, and, hence, to prevent its escape to the overlying water column. Colourless sulphur bacteria are gradient-type microorganisms (Nelson & Jannasch 1983; Nelson et al. 1986; Strohl 1989) that are capable of significantly narrowing and stabilizing the $H_2S/O_2$ interface (Jörgensen 1982; Jörgensen & Revsbech 1983). Shifts of this interface, associated with changes in bottom water oxygen levels, mat burial, or small-scale productivity variations, would promote recurrent pulses of dissolved phosphate, just beneath the zone of active mat growth, possibly creating the conditions of supersaturation necessary to initiate phosphate precipitation. Intense metabolic oxidation of hydrogen sulphide along a narrow $H_2S/O_2$ interface may also aid the precipitation of phosphate due to local acidification of pore waters. Lowered pH values and low carbonate alkalinities at $H_2S/O_2$ interface may catalyze the precipitation of calcium phosphate salts (Van Cappellen & Berner 1991).

The development of favourable conditions for calcium phosphate precipitation is not necessarily confined to gradient-type microbial mats capping anoxic and oganic-rich sediment columns. These conditions are also likely to develop in microbial mats occupying shallow and well-aerated marine environments. These latter mats are usually thick and complex biological structures, which show a stratification of zones dominated by different mat-building (mostly photosynthetic) and decomposing organisms (for references, see Cohen et al. 1984; Cohen & Rosenberg 1989). Vertical changes of metabolic activity and organic matter synthesis and mineralization across this stratification result in downward-increased oxygen consumption and the formation of sharp compositional gradients within the microbial mat fluids. In many cases, intense degradation of organic matter at the base of the mats exhausts the free oxygen and promotes dissimilatory sulphate reduction, leading to the development of $H_2S$ "pillows" at the mat-sediment interface. The zone of hydrogen sulphide oxidation at the edge of such "pillows" has been shown to initiate calcium phosphate precipitation in laboratory cultivated microbial mats, if a sufficiently high level of dissolved phosphate exists (Krajewski & Krumbein, unpublished). In these experiments, the solid phosphate developed rapidly via a metastable and poorly crystalline precursor phase, similar to the ACP of Van Cappellen (1991), and transformed into apatite in a period of a few weeks. The ongoing phosphate precipitation led to mineral preservation of the subsurface mat zone, through the coating of mat organisms with a tight apatitic deposit (Fig. 9). A detailed understanding of the mat phosphatization

process requires further study, although it appears that the redox processes in the mat microenvironment were involved in triggering the precipitation process. If confirmed, this mechanism might explain the formation of ancient phosphatic stromatolites (see section 3). There are no known modern phosphatic stromatolites, because most contemporary phosphogenic environments do not provide adequate conditions for the development of stable stromatolite-building communities. However, recently revealed phosphate-bearing cyanobacterial mats in Tahiti atolls might serve as an example of such a biosedimentary system (C. Jehl, personal communication).

Many papers have been written on the possible role of microorganisms as crystallization sites for calcium phosphate. Based on morphological arguments, apatite paticles in both modern and ancient phosphorites have been interpreted as phosphatized bacteria (see section 3). It is well established that microorganisms participate in the precipitation of a spectrum of minerals in aquatic environments (for recent reviews, see Simkiss & Wilbur 1989; McLean & Beveridge 1990). Most microbial mineralization products form extracellularly and are influenced by the structure and functions of cell membranes (Mann 1989; Simkiss & Wilbur 1989). It is known that functional groups emerging from the wall and membranous macromolecules provide favourable binding sites for calcium ions and, hence, may promote the nucleation of calcium minerals on cellular structures (Eliott 1985). Whether such a cellular mechanism actively accelerates apatite deposition in sediments remains a subject of controversy. In our opinion, the availability of surface sites,
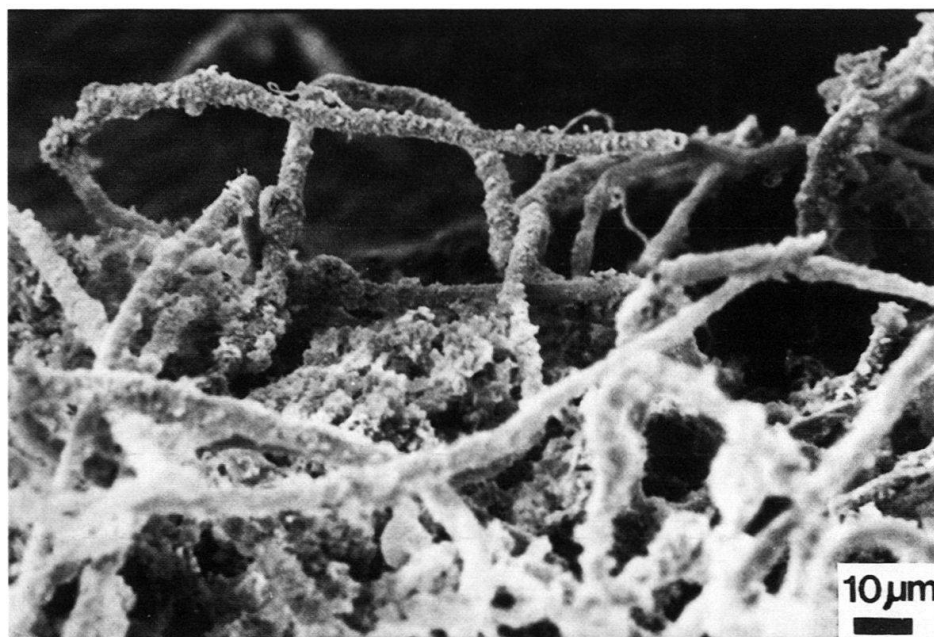


Fig. 9. Experimentally phosphatized microbial mat dominated by filamentous cyanobacteria *(Oscillatoria, Microcoleus)*. Cyanobacterial filaments are coated with thin layers of deposited phosphate, which originated as a result of rapid precipitation of an amorphous calcium phosphate phase within the mat microenvironment. The presence of this phase was documented by a combined X-ray diffraction (XRD) and infra-red spectroscopy (IR) analysis. Using XRD, carbonate fluorapatite was identified as having developed as a result of the reorganization of the precursor structure. The extracellular phosphate deposit maintains the morphology of the filaments after lysis and decomposition of cyanobacteria, which leads to the formation of apatitic hollow-tube structures in the mat meshwork. SEM photomicrograph; sample after critical-point drying procedure. Krajewski & Krumbein (unpublished materials); sample No. H10–2b. Photo by K.P. Krajewski.

organic or inorganic, for nucleation of calcium phosphate may not be a limiting factor in the deposition of sedimentary phosphorites. The formation of apatite via poorly organized calcium phosphate precursor phases, inferred for many phosphogenic environments, is a rapid process that takes advantage of any substratum available. The situation can clearly be illustrated by the results of laboratory experiments of bacterial apatite formation (Lucas & Prévôt 1981, 1984, 1985; Vaillant 1987; El Faleh 1988; Hirschler 1990; Hirschler et al. 1990a, 1990b). In these experiments, the development of bacteria was stimulated by phosphorus-rich organic compounds (ribonucleic acid) in the presence of a calcium donor (usually calcium carbonate). Bacterial decomposition of organic compounds liberated phosphate which subsequently precipitated with calcium to produce a solid phosphate phase, mostly carbonate fluorapatite (Prévôt et al. 1989). The detailed analysis of ultrastructures of this apatite suggests its formation via amorphous-like precursor phases (Fig. 10), which is consistent with high phosphate supersaturation levels attained in the experiments. The observed patterns of the phosphate deposit provided no evidence of preferential nucleation of apatite on bacterial substratum. The apatite was noted to develop on or close to bacterial cells as well as on mineral substrata devoid of bacteria (Vaillant 1987; Hirschler 1990). Where found in association with bacteria, the apatite always formed extracellular deposits around bacterial cells (Fig. 11). The mineral structures encapsulating the cells were made of apatite without any clearly defined crystalline form (Fig. 12). The presence of apertures in the apatitic capsules suggests that the formation of phosphatic coatings on bacteria occurred during an active metabolic stage of the cells. The common development of phosphatized bacterial structures was observed
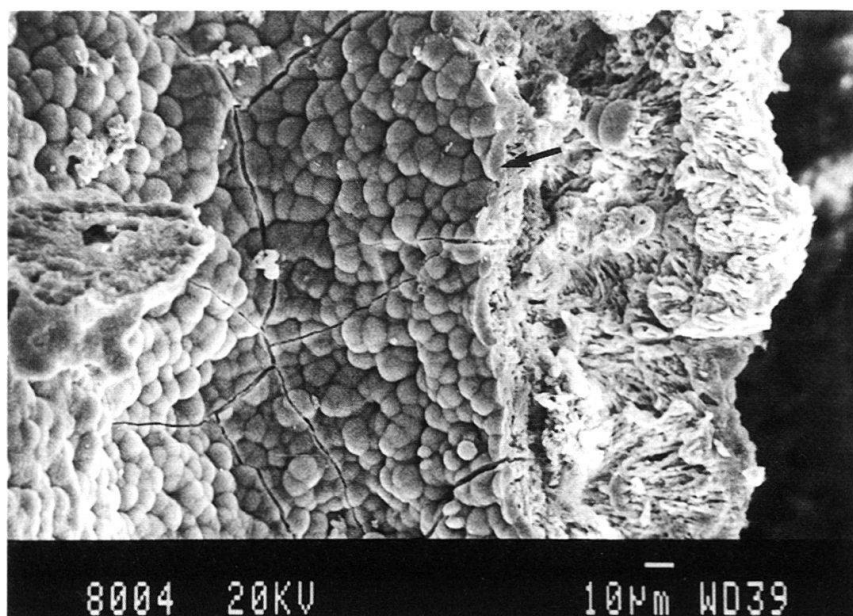


Fig. 10. Apatite rim cement (arrow) developed directly on the mineral substratum (coral septum) in the course of a bacterial phosphate precipitation experiment (Lucas & Prévôt 1985). The globular ultrastructure of the apatite reflects the rapid formation of a poorly ordered precursor phase involving a high concentration of nucleation sites on the mineral surface. This mechanism is consistent with a high level of the supersaturation of the medium, attained by the intense bacterial degradation of ribonucleic acid (phosphorus source). SEM photomicrograph; sample No. J.L. 15. Photo by K.P. Krajewski.
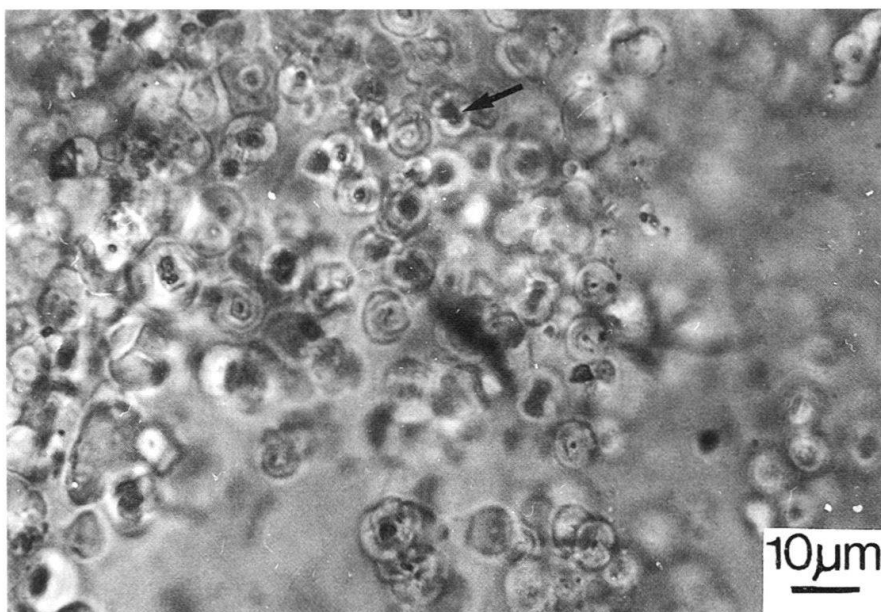
Fig. 11. Apatitic coatings developed around bacterial cells (arrow) in the course of a bacterial phosphate precipitation experiment (Lucas & Prévôt 1985). TLM photomicrograph, normal light; sample No. J.L. 816F. Photo by K.P. Krajewski.
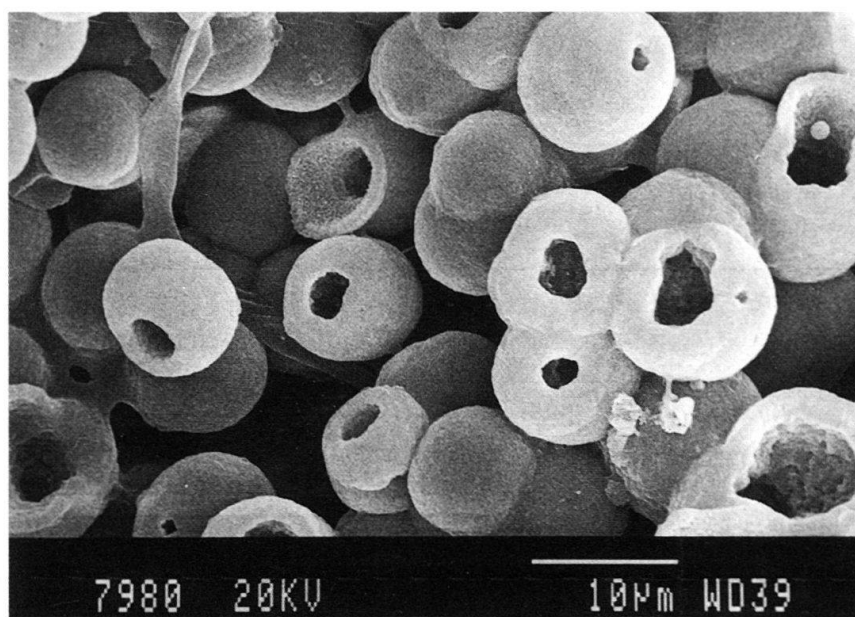


Fig. 12. Apatitic capsules developed around bacterial cells in the course of a bacterial phosphate precipitation experiment (Lucas & Prévôt 1985). Common apertures in the apatitic capsules indicate that the phosphate accretion on bacteria occurred during active metabolic processes of the cells. SEM photomicrograph; sample after artificial removal of bacterial matter. Sample No. J.L. 816F. Photo by K.P. Krajewski.

in experimental situations where bacteria provided the dominant (or the only) available substratum, or where they formed tight biofilms on mineral surfaces.

A similar pattern of phosphate deposition was noted in the course of experimental phosphatization of microbial mats (Krajewski & Krumbein, unpublished). The amor-

phous phosphate phase precipitated randomly on all the available substrata present within the mat. However, the predominance of biological substrata in the mat environment contributed to the concentration of solid phosphate (and then apatite) on the microbial bodies.

In the inorganic nucleation experiments of Van Cappellen (1991), the spontaneous precipitation of the $OCP_p$ precursor was not found to be sensitive to the addition of mineral substrates. In fact, the nucleation of the precursor was very much akin to homogeneous nucleation. In the course of time, however, the precipitate agglomerated and adhered to the available subtrata, including the walls of the reaction vessels, added mineral grains and even the teflon-coated stir bars.

In the light of common overinterpretations given in the geological literature, we believe the following statements best represent the current state of knowledge of the relationship between microorganisms and authigenic apatite formation:

1. Microorganisms affect the production, storage and distribution of reactive phosphate in sediments. As such, they are instrumental in determining where and when calcium phosphate precipitation is initiated in a sediment. Microbial activity, in turn, is modulated by environmental conditions, including bottom water oxygen levels, supply and reactivity of deposited organic matter, bioturbation and sedimentation rate.

2. Microbial reactions are largely responsible for the chemical composition of the pore water environment by affecting the actual concentrations of chemical species, their ionic strenghts and activities, and modulating redox conditions and pH-dependent state parameters like alkalinity. Pore water chemistry has a predominant effect on the precipitation pathway of apatite formation (i. e. with or without a precursor). It further controls the kinetics of the transformation of precursors into apatite and the crystal growth of apatite.

3. There is no evidence that cellular bodies are a necessary or even preferential substratum for the formation of apatite. Nevertheless, the abundance of microbiota in the precipitation environment leads to the common deposition of apatite on microorganisms.

## 3 Biological activity and apatite formation in the fossil record

The impact of biological processes on the formation of apatite has, so far, only been investigated in phosphorus-rich sedimentary rocks. Little is known about the biological control on early phosphorus transformations in sedimentary settings showing a "normal" content of authigenic apatite, i. e. corresponding to $\leq 0.1$ wt.% $P_2O_5$ total rock. However, there is reason to suppose that the two types of apatite occurrence recorded in sedimentary rocks involve different types of mineral formation (see section 2). In non-phosphogenic sedimentary settings, the biological involvement in dispersed apatite formation seems to be mostly restricted to microbially-mediated liberation of phosphate from deposited phosphorus containing particulate matter. The concentrated apatite formation in phosphorites, on the other hand, reflects a strong microbial influence during all major steps of the benthic phosphorus transformation, including the phosphorus solubilization, concentration and mineral precipitation. Much of the discussion so far has dealt with evidence from modern depositional environments. The evidence of benthic microbial activity in ancient phosphogenic environments is discussed in this section.

*Phosphorus and organic carbon association*

The stratigraphical and facies association of the phosphorus-rich and organic carbon-rich rocks is widely recognized in the geological column (e. g. Bodelle et al. 1980; Sheldon 1981; Loughman 1984; Slansky 1986; Yanshin & Zharkov 1986). It confirms a predominant role of biological productivity in determining the zones of concentrated apatite deposition. Marine phosphate deposits fueled by a supply of inorganic particulate phosphorus seem to be a less common, but as yet not sufficiently documented, sedimentary system (Glenn & Arthur 1990; Glenn et al. 1994).

Sedimentary rocks of the phosphogenic facies settings have an organic carbon content ranging from tenths of a percent to approximately 20% (e. g. Belayouni 1983; Samb 1983). In these rock sequences, an increase of organic carbon content is, in general, associated with a drop in the mineral phosphorus content, although detailed relations may show more complex patterns. For instance, average organic carbon values of phosphorites and associated organic-rich shales of the Tertiary Ouldad Abdoun basin of Morocco are 6% and 17%, respectively (Benalioulhaj 1989). A similar association from the Cambrian of Georgina Basin in Australia shows average values of 1% and 3–9% (Sandstrom 1986), and that of the Permian Phosphoria Formation in the Western U.S., 2.5% and 10% (Maughan 1980). The organic carbon distributions in these sequences are believed to reflect differential preservation of sedimentary organic matter, with its severe microbial degradation and oxidation in environments of intense phosphogenesis, and its enhanced burial in anoxic, organic-prone environments (McArthur 1986; Meunier-Christmann et al. 1989; Belayouni et al. 1990).

*Organic matter*

Most of the fossil phosphorites investigated by means of organic geochemical methods show the presence of sedimentary organic matter of indigenous marine origin (Powell et al. 1975; Sandstrom 1980; Belayouni & Trichet 1980a; Belayouni 1983; Benalioulhaj 1989; Benalioulhaj & Trichet 1990; Fikri 1991). This type of organic matter is identified by the elemental composition and pyrolitic characteristics of kerogen and/or humic substances and by the nature and composition of extractable organic fractions. On purely geochemical grounds, it is, however, difficult to elucidate whether the sedimentary organic matter orginated from planktonic or benthonic productivity. Paleoenvironmental reconstructions of ancient phosphogenic systems show structural and bathymetric configurations that would suggest planktonic productivity, although some shallow to semi-emergent phosphogenic environments may have been especially prone to proliferation of benthic autotrophs (e. g. phosphatic facies of Georgina Basin, Southgate 1986). The organic matter preserved in phosphorites exhibits features of its intense microbial degradation and oxidation (Sandstrom 1986; Meunier-Christmann 1988). In highly condensed phosphorite horizons, this degradation may even lead to the near-complete decomposition of indigenous organic matter, and the preservation of only residual organic fractions (Krajewski 1989). In many ancient phosphorites, the oxidative microbial alteration of oganic matter is expressed by a high proportion of humic compounds in the fossil organic fractions and by a set of biomarker compounds.

*Humic compounds*

Microbial degradation of sedimentary organic matter leads to the development of polymer fractions of carbohydrates, proteins, lipids and lignin-derived polyphenols, which condense to form aliphatic and aromatic complexes, termed humic compounds (Rashid 1985). These compounds are, in general, resistant to further microbial decay and become preferentially buried in sediments. The common occurrence of humic compounds in ancient phosphorites has only been revealed relatively recently. Nevertheless, they are now recognized as one of the fundamental features of phosphorites, reflecting both a dominant type of environmental organic matter transformation and a peculiar preservational regime linked to the phosphate mineral formation.

The abundance of humic compounds in the organic fraction of phosphorites (up to 86% Humic Acid Carbon in the Total Organic Carbon, Belayouni et al. 1990; Nathan 1990) allows their extraction and detailed geochemical study. Various methods, including elemental analysis of purified humic acids, molecular analysis of the chloroform extract, IR spectroscopy, thermogravimetry, X-ray diffraction and E4/E6 light-absorption have been used in an attempt to reconstruct the structural organization of the humic compounds and their origin (for references, see Nathan 1990; Trichet et al. 1990). The results of these studies confirm that the organic matter deposited in ancient phosphogenic environments was of marine, mostly phytoplanktonic origin. However, the humification pathways, as well as the structural evolution of the humic substances, remain much less clear.

The presence of humic compounds in phosphate deposits as old as the Cambrian (Sandstrom 1980, 1986) and their abundance in Mesozoic and Tertiary phosphorites seem to reflect peculiar diagenetic conditions leading to the preferential preservation of humified organic matter in association with phosphate minerals (Nissenbaum 1979; Trichet et al. 1990). The formation of organo-mineral aggregates where humic compounds are sorbed on surfaces of minute apatite particles seems to account for this preservation (Trichet & Défarge 1994). Flexible morphologies of external chains of humic acids (polyelectrolytic, often polypeptidic chains) inhibit mineral crystallization and provide conditions favourable for the development and preservation of poorly crystalline organo-mineral aggregates (Sarig et al. 1975; Ghosh & Schnitzer 1980). This relationship has been proven experimentally for the apatite-humic acid association (Inskeep & Silvertooth 1989; Fréche & Lacout 1992). The enhanced preservation of humified organic matter in phosphorites could, therefore, be related to the poor crystallinity and compactness of phosphatic pellets and grains.

In our opinion, emphasis of further research should be placed on the humic substances in phosphorites, especially since there are general similarities in the development of this class of compounds in both modern and ancient phosphogenic environments (e. g. Poutanen & Morris 1983; Sandstrom 1990). In particular, the role of humic compounds in controlling phosphate nucleation sites and crystal morphology and size awaits detailed study. It is known that acidic amino-acids may promote the nucleation of calcium minerals, both carbonates and phosphates (Veis & Perry 1967; Mitterer & Cunningham 1985; Addadi & Weiner 1985; Trichet et al. 1990). Significantly high concentrations of aspartic and glutamic acids in humic substances of some phosphorites have been demonstrated (Belayouni & Trichet 1980b; Belayouni 1983; Trichet et al. 1990), although the detailed relationship between these acids and the apatite precipitation remains poorly understood.

*Biomarkers*

Unless severely oxidized, sedimentary organic matter of ancient phosphorites has been acknowledged a remarkable reservoir of biomarkers. Consequently, several detailed studies have attempted to provide information on these compounds. Most studies have been focused on hydrocarbon and fatty acid distributions (Powell et al. 1975; Amit & Bein 1982; Bein & Amit 1982; Belayouni & Trichet 1984; Sandstrom 1986; Benalioulhaj 1989; Belayouni et al. 1990, Fikri 1991), while only limited effort has yet been directed towards specific compound groups, such as amino-acids or amino-sugars (e. g. Belayouni & Trichet 1980b).

Extensive microbial processing of sedimentary organic matter is reflected in characteristic hydrocarbon signatures. The n-alkanes usually show a unimodal smooth distribution in the range $n-C_{15}$ to $n-C_{23}$ (Fig. 13) or a bimodal distribution. In the first case, the genesis of hydrocarbons is interpreted as the result of a microbial degradation of algal (phytoplanktonic) organic matter (Powell et al. 1975; Sandstrom 1980, 1986; Belayouni & Trichet 1984; Benalioulhaj 1989). In the second case (bimodal distribution), the first hump, centered around $n-C_{17}$ is attributed to algal-derived hydrocarbons, while the second hump, $n-C_{18}$ to $n-C_{29}$, is characterized by the absence of odd to even predominance (Fikri 1991). This feature is considered to reflect bacterial alteration (the so-called bacterial conversion) of marine organic matter (Gassmann 1982). The possible absence of light hydrocarbons in the phosphorite extracts can also be explained by their severe degradation by bacterial communities.

Acyclic isoprenoids (mostly pristane and phytane) are commonly present in the extract fraction (Fig. 13). They could either result from intense biological diagenesis of chlorophyll, or reflect the contribution of certain groups of bacteria (e. g. anaerobic photosynthetic or methanogenic bacteria) to the organic matter. The presence of isoprenoids with higher and lower carbon numbers than those of pristane and phytane suggests, however, the dominant role of bacteria in providing this class of compounds. High molecular weight cyclic hydrocarbons (steranes, hopane triterpanes) are commonly present in the organic matter of phosphorites. Their presence confirms both the phytoplanktonic origin of this organic matter and the role of benthic microbial communities in its decomposition (Sandstrom 1980; Belayouni 1983). Their absence, or a low content, is interpreted as a result of intense microbial degradation (Sandstrom 1986).

*Phosphatic microbial fabrics*

Benthic microbial activity in ancient phosphogenic environments can be indicated by imprints left by synsedimentary microbiota on mineral fabrics of phosphorites. The microbial fabrics have long been recognized in phosphorites (Cayeux 1936; Oppenheimer 1958; Riggs 1979), but the increased use of scanning electron microscopy in the last ten years has provided an abundance of information on their organization and ultrastructure (e. g. Mitrov et al. 1987).

These studies show that the microbial fabrics developed as a result of the rapid formation of authigenic apatite, which preserved remnants of various benthic communities inhabiting the topmost layers of phosphogenic sediments. Despite the diversity of the fabrics, the microbial fossils seem to reflect a common mechanism of preservation. This
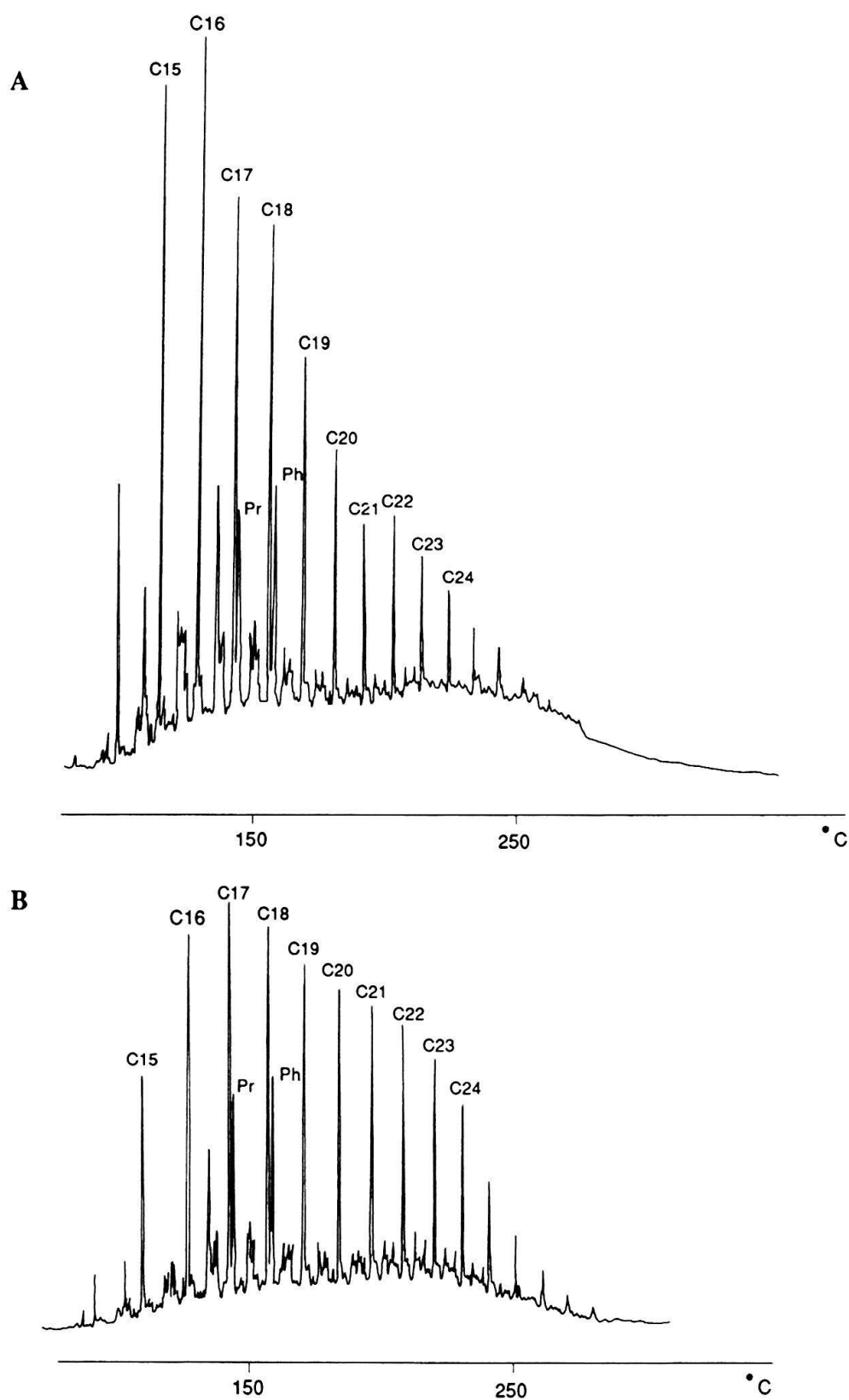
Fig. 13. Chromatograms of saturated hydrocarbons from the Upper Cretaceous – Tertiary phosphorites of the Ouldad-Abdoun basin of Morocco. C15 to C24 – numbers of carbon atoms in normal alkane chains; Pr – pristane; Ph – phytane. A: sample S4–101; B: sample S4–108. For other explanations see text. After Benalioulhaj (1989).

mechanism involved *extracellular precipitation of apatite* and led to the formation of external moulds of microbial bodies (see section 2). Depending on the nature of subsequent diagenetic processes, the apatitic moulds could retain remnants of the original microbial matter (mostly wall and membranous structures), remain empty after decomposition of the organic matter or show various mineral infillings. A lack of compactional deformation of the moulds allows identification of their internal morphology as imprints of the original organisms. Therefore, on the basis of morphology, informal categories of microfossils can be recognized, and assigned to major groups of microorganisms. Several such categories have been so far recognized, and assigned to *(i)* cyanobacteria, *(ii)* other bacteria and *(iii)* fungi. The presence of filamentous cyanobacteria is evidenced by meshworks of regular tubular structures without branchings, and with internal diameters ranging from 2–3 µm to approximately 10 µm (Soudry & Champetier 1983; Soudry 1987; Mitrov et al. 1987). The occurrence of coccoid cyanobacteria has also been reported (Krajewski 1984; Soudry & Lewy 1988; Soudry 1992), although here the microstructural evidence is much more speculative. Branching tubular forms that show common variations of internal diameter, chlamydospore-like structures and regular thickenings or chambers have been interpreted as representing remnants of fungal communities (Dahanayake & Krumbein 1985; Bréhéret 1991). The identification of bacterial fabrics is most difficult, because there are no unequivocal morphologic cirteria which would help in their recognition. In our belief, only mineral fabrics showing morphologies of apatite frameworks similar to phosphate-preserved bacteria known from laboratory experiments could reasonably be considered to be of bacterial origin (Fig. 14 and 15, compare with Fig. 11 and 12). These phosphatic fabrics consist of agglomerations of empty or variably infilled apatitic capsules, showing ovoidal to rod-like shapes, and external dimensions up to a few µm (Senkovsky 1982; Prévôt & Lucas 1985; Zanin et al. 1985, 1987; Soudry & Lewy 1990). In these fabrics, open apertures in the apatitic capsules are typically observed.

The proliferation of benthic cyanobacteria was limited to shallow phosphogenic paleoenvironments, allowing a concentration of biological productivity on the seabed. Campanian phosphorites of the Mishash Formation in Israel provide a well-known example of such an environment (Soudry & Champetier 1983). The production of cynobacterial mats and their penecontemporaneous phosphatization and reworking aided the formation of a high-grade granular phosphorite cemented by a filamentous phosphatic matrix (Soudry 1987).

The available data are too scarce to elucidate the distribution and importance of other microbial fabrics in phosphorites. However, since the proliferation of heterotropic bacteria and fungi marks high rates of organic matter decay, their traces could be expected in ancient phosphorites ragardless of their paleoenvironmental position. For instance, Bréhéret (1991) showed an example of recurrent development and phosphatization of fungal mats in the mid-Cretaceous phosphatic shales of the Vocontian basin, and Dahanayake & Krumbein (1985) reported the abundance of fungal mat remains in the Tertiary granular phosphorites of Morocco.

Sedimentary sequences with laterally continuous beds or layers of pristine phosphate may potentially provide valuable insights into the composition and spatial distribution of benthic microbial communities in phosphogenic paleoenvironments. The layers of pristine phosphate represent non-steady state events of apatite emplacement in sediments, that were excluded from subsequent dynamic and/or biological reorganization. Therefore, they
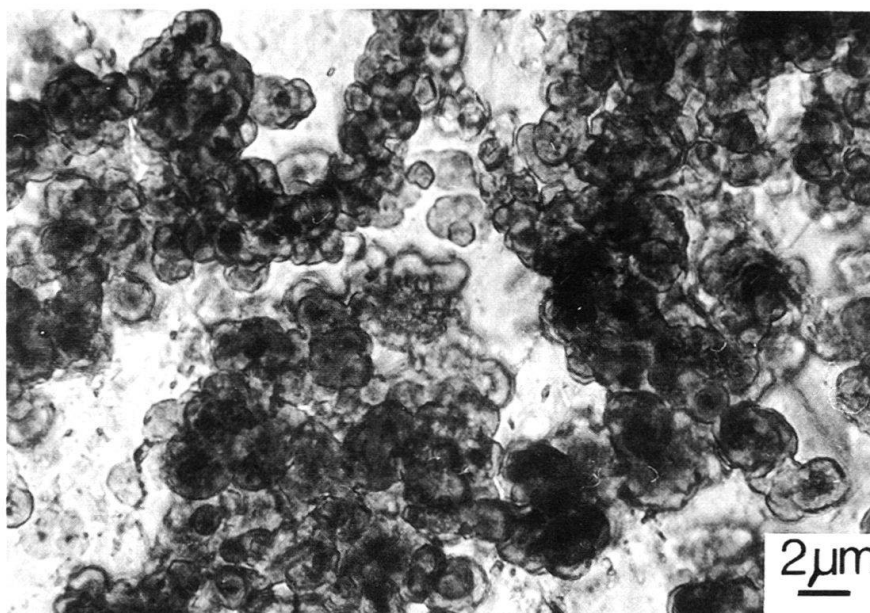
Fig. 14. Microbial fabric in a pristine phosphate layer from the Triassic Bravaisberget Formation of Spitsbergen. The fabric is defined by loose aggregates to apatitic globules (gray) encapsulating remnants of microbial cells (black). It developed as a result of rapid phosphate precipitation on coccoid microorganisms (probably bacteria), that inhabited the surface layer of an organic-rich and phosphogenic sediment column. TLM photomicrograph, normal light. Photo by K.P. Krajewski.
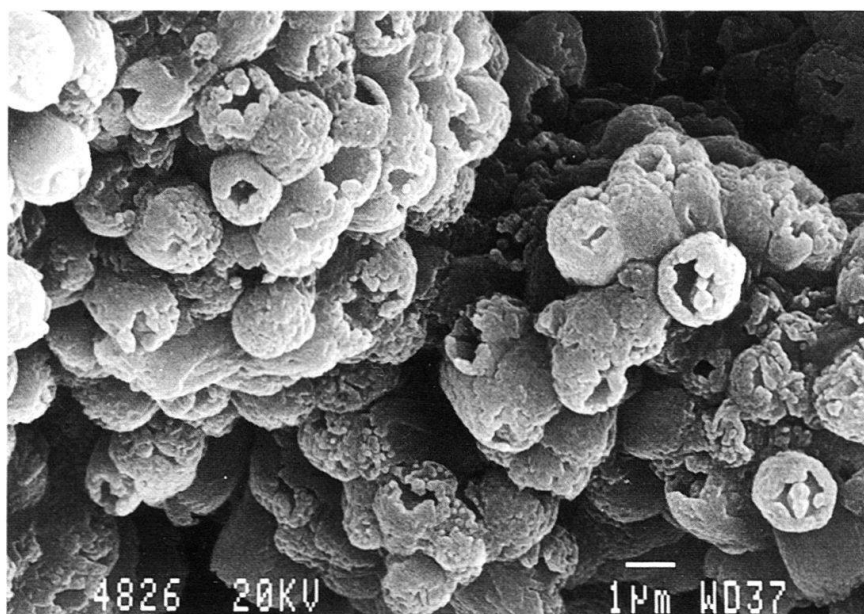


Fig. 15. Detail of the phosphatic microbial fabric shown in figure 14. Aggregates of apatitic capsules showing open apertures aligned towards the open pore space reflect rapid deposition of phosphate on a community of coccoid microorganisms (probably bacteria). SEM photomicrograph. Photo by K.P. Krajewski.

are likely to preserve patterns of the original distribution of benthic microbiota in the topmost parts of ancient phosphogenic sediment columns, as shown for example in the work of Reimers et al. (1990) on the ultrastructure of pristine phosphate layers in the Miocene

Monterey Formation of California. By combining geomicrobiological and sedimentological methods, these authors assigned the observed community remnants to colourless filamentous sulphur bacteria, highlighting the association of this group of microorganisms with phosphate authigenesis in ancient organic-rich sediments (see section 2). Krajewski & Krumbein (unpublished) also used microfabric sequence analysis of indigenous phosphatic crusts to document depth zonation of microbial communities in the surface layers of organic-rich and phosphogenic sediment columns in the Triassic Bravaisberget Formation of Spitsbergen.

In addition to the fabrics described above, many phosphorites show traces of the endolithic activity of microorganisms on hard sediment surfaces. Microborings typical for cyanobacteria (Soudry 1979) and fungi (Krajewski 1981a) have been recognized. Intense endolithic activity of microbiota on sedimentary grains and consequent apatite precipitation in microboring systems (the so-called bio-phosphomicritization) is believed to have produced at least a portion of structureless peloids in some granular phosphate deposits (Soudry & Nathan 1980).

The other result of the microstructural studies of phosphorites was the discovery that many phosphatic matrices and grains are composed of minute apatite particles morphologically resembling bacteria (see e. g. Baturin & Dubinchuk 1979; Bremner 1980; Baturin 1983; Baturin et al. 1985; Mullins & Rasch 1985; Rao & Nair 1988; Lamboy 1994, for seafloor phosphorites; and Zimmerle 1982; Garrison et al. 1987; Garrison & Kastner 1990; Lewy 1990; Lamboy 1993, for some ancient examples). These particles are usually micronsized rods, globules or spindles, made of compact apatite without any clearly defined crystalline form (Fig. 16). This observation led some authors to suppose that the apatite particles represent phosphate-replaced bacterial cells (O'Brien et al. 1981; Lamboy & Monty 1987; Lamboy 1990a, 1990b). According to this hypothesis, certain bacteria in phosphogenic environments were capable of concentrating apatite intracellularly, thereby controlling its distribution in the sediment and affecting the ultrastructure of the phosphatic fabrics. However, no clear criteria of bacterial origin of the apatite particles have been presented, neither has the mechanism of bacteria replacement by apatite been documented. To our present knowledge, there is no convincing evidence for direct intra-cellular apatite deposition in phosphogenic environments. The "bacteria-like" shapes of apatite particles could be the result of rapid nucleation events in the pore water medium (see section 2). This has been demonstrated in laboratory experiments, which show a broad spectrum of phosphate precipitates resembling very closely the "bacterial" morphologies of natural apatites (Vaillant 1987; El Faleh 1988; Hirschler 1990; see also Gulbrandsen et al. 1984).

*Phosphatic stromatolites*

Phosphatic stromatolites provide examples of close spatial association of benthic microbial activity and apatite deposition in ancient phosphogenic environments. These biosedimentary structures reflect localized developments of microbial mats which, by their growth and metabolic activity, contributed to the formation of laminated, usually highgrade, phosphatic rock bodies (e. g. Krajewski 1981b; Kumar & Muller 1988; Tewari 1993; Martín-Algarra & Vera, in press). However, since modern analogs of phosphatic stromatolites remain unknown, the detailed nature of processes affecting apatite concentration in these structures is surrounded by much controversy.

Fig. 16. Matrix of a pristine phosphate layer from the Triassic Bravaisberget Formation of Spitsbergen. Densely packed apatite particles imply a rapid phosphate precipitation event that produced a very high concentration of nuclei in the original porosity of an organic-rich sediment. The particles show rod-like shapes and are made of apatite without any clearly defined crystalline form. SEM photomicrograph. Photo by K.P. Krajewski.

In section 2, we attempted to demonstrate that the concentration of apatite within a dense benthic community may reflect an interplay of several distinct microbial effects. These include the transitory fixation of phosphorus, the regulation of dissolved phosphate liberation and the modification of the chemistry of the microenvironment. All these effects probably contributed to phosphate authigenesis in stromatolite-building communities, but the basic prerequisite of this process must have been a significant supply of phosphorus from an external environment. In this respect, phosphatic stromatolites could be regarded as localized and efficient microbial traps of phosphorus circulating within ancient depositional systems.

The vast majority of phosphatic stromatolites occur within the limits of two distinct phosphogenic provinces: (*i*) the Precambrian-Cambrian Asian-Pacific province and (*ii*) the Mesozoic Mediterranean province. This distribution reflects a coincidence of the regional development of phosphogenic conditions in the provincial sedimentary basins, and the development of local environments that favoured proliferation of stromatolite-building communities. The environments prone to microbiota proliferation and associated microbial manifestations were markedly different in the two provinces (see below). However, the basic features of apatite development in the stromatolites are similar, and independent of the geological age and paleoenvironmental location. Three of these features are of some significance with regard to the biological controls on apatite formation.

First, the authigenic apatite is always concentrated within the stromatolitic bodies, and is not observed to straddle their boundaries, either horizontally or vertically. This implies a rapid decline of conditions favouring apatite precipitation at the boundary between the original stromatolite microenvironment and the surrounding bethic environ-

ment. Second, the content of authigenic apatite fluctuates within the stromatolites according to the original stromatolite bio-lamination, suggesting that the intensity of apatite deposition was mainly definded by cyclic variations in the activity of stromatolite-building communities. Third, phosphatic stromatolites show the presence of other authigenic minerals, of which pyrite and/or glauconite are typical accessory components. Their distribution usually follows the pattern of the original bio-lamination, inferring the (temporal) development of reducing or nearly reducing conditions in the stromatolite microenvironment. This, again, suggests a close association between microbial redox processes and apatite deposition.

### Precambrian-Cambrian

Precambrian to Cambrian phosphatic stromatolites are known from numerous localities in Siberia, Kazakhstan, China and Mongolia (Bushinski 1964, 1969; Krasilnikova & Paul 1983; Eganov 1988), India (Banerjee 1971; Valdyia 1972; Chauhan 1979, 1980; Banerjee et al. 1980; Chauhan & Sisodia 1981; Tewari 1981a, 1981b, 1984a, 1984b, 1984c, 1989, 1991a, 1991b, 1993; Kumar & Muller 1988) as well as from Australia (Southgate 1980, 1986; Schmitt & Southgate 1982). These stromatolitic occurrences are found in the phosphatic to carbonate facies associations indicative of shallow-marine restricted environments, which show broad variations of depositional regime from submergent to emergent. Shallow marine environments of low terrigenous input provided typical niches for the Precambrian-Cambrian biotas, which concentrated the reactive phosphorus at the margins of landmasses and provided a driving force for the early phosphogenic system development (Awramik 1971; Schopf & Walter 1982; Cook & Shergold 1986).

Precambrian-Cambrian stromatolitic ecosystems exhibited a widespread predominance of precipitation of carbonate minerals under most shallow-marine conditions (Maslov 1960; Awramik et al. 1976). Carbonate deposition was directly related to carbon dioxide photoassimilation and led to the widespread deposition of limestone and/or dolostone stromatolitic rocks (Monty 1973; Awramik 1984). Stromatolitic phosphorites were, therefore, likely to form in environments in which an intense phosphorus supply to localized stromatolitic communities suppressed the microbial precipitation of carbonate minerals (Banerjee et al. 1986). Purely apatitic stromatolites are, in fact, seldom observed in the Precambrian-Cambrian sedimentary record. Most phosphatic stromatolites display a noticeable calcium carbonate admixture, suggesting an interplay of the phosphatization and calcification processes during their growth (Fig. 17). Changes of the dominant stromatolite mineralogy from apatitic to carbonate and vice versa, which are discordant to the original lamination of stromatolitic structures, are observed in some phosphogenic facies, mostly in Cambrian settings (Southgate 1986; Eganov 1988). These facies represent semi-emergent to emergent (tidal) terminations of marine phosphorites, which suggest a pronounced heterogeneity of the sedimentary distribution and circulation of phosphorus during the stromatolite growth (Southgate 1988). The commonly observed mineral pattern in the Precambrian sequences consists of a regular alternation of apatitic and carbonate laminae (or sets of laminae) in vertical stromatolite sections (Banerjee 1971; Tewari 1993b). This pattern could be related to cyclic (?seasonal) changes of ecosystem activity, that influenced both the phosphorus supply to stromatolitic communities and the intensity of microbial mineralization processes. The detailed mechanism, by which apatite was

recurrently emplaced in the stromatolitic structures, is not precisely understood, due to the loss of primary mineral fabrics caused by diagenetic recrystallization. The alternating precipitation of apatite and carbonate in the mat microenvironment as well as the repeated replacement of microbially calcified laminae by apatite have received some support from petrological studies of stromatolites (Banerjee 1971; Valdiya 1972; Chauhan 1979; Schmitt & Southgate 1982; Tewari & Qureshy 1985; Eganov 1988; Tewari & Joshi 1994).

Stromatolitic phosphorites of the Precambrian-Cambrian are voluminous and represent major deposits in the Asian-Pacific province (Bushinski 1969; Eganov 1988). The distinct morphologies of the stromatolites and the broad spectrum of microbial fossils point to abundant and specialized microbial ecosystems contributing to stromtolitic apatite deposition (Shukla et al. 1986; Tewari 1991a, 1991b, 1993). A dramatic decline of marine stromatolite-building communities in the Ordovician, related to the overwhelming development of metazoans, confined the formation of phosphatic stromatolites to peculiar ecological niches in younger phosphogenic systems.



Fig. 17.  Proterozoic phosphatic stromatolites from Udaipur, Rajahstan (India) provide an example of an early phosphogenic system, in which the environmental phosphorus was preferentially immobilized in localized microbial-mat communities. The alternating apatitic (black) and carbonate (white) laminae point to an interplay of the phosphatization and calcification processes during the growth of stromatolitic structures. (Pencil for scale) Photo by V.C. Tewari.

*Mesozoic*

Late Mesozoic phosphatic stromatolites occur at numerous locations along the northern margin of the Mediterranean Tethys, in the Betic Cordillera of S. Spain (Martín-Algarra & Vera, in press; Vera & Martín-Algarra, in press), in northern subalpine units of S. France (Delamette 1981, 1986), in the Swiss, Austrian and Bavarian Helvetic Alps (Föllmi & Ouwehand 1987; Ouwehand 1987; Föllmi 1989, 1990; Salomon 1989), and in the Western Carpathians (Krajewski 1981a, 1981b, 1983, 1984). They are also known from the adjacent epicontinental basins, mostly in the Polish Jura Chain (Golonka & Rajchel 1972; Marcinowski & Szulczewski 1972; Marcinowski 1974), and from some southern alpine units in Italy (Massari & Medizza 1973) and Greece (F. Pomoni-Papaioannou, written communication). These stromatolites are typically found in stratigraphically condensed sequences, which reflect drowning episodes of carbonate platforms at the Tethyan margin and rapid transgressive pulses in the adjacent epicontinental seas. They formed under submarine hiatal conditions, frequently encrusting the submerged rock substrata or extensive hardgrounds in common association with sessile oganisms (arenaceous and calcitic formaninifera, serpulids, solitary corals). The associated sediments range from pelagic, fossiliferous to glauconitic limestones indicative of slow and/or episodic sediment accretion and prolonged diagenesis at the seafloor. The phosphatic stromatolites are small structures, showing a high variability in spatial organization and fabric. They developed as a result of the interplay of two different mechanisms, i. e. the trapping and binding of fine detrital sediment by microbial mats, and the precipitation of apatite within the mats (Krajewski 1981b). No biocalcification mechanism has been revealed to contribute to the formation of these stromatolites. Dominantly apatitic stromatolites tend to be composed of minute microlaminated units (frequently called microstromatolites), which define both the structure and fabric of the authigenic phosphate deposit (Fig. 18).

The facies associations and sedimentological characteristics of Late Mesozoic stromatolites point to peculiar environmental conditions constraining the paleoecological niche of the stromatolitic microbial communities. Data accumulated so far pesent severe interpretational problems in reconstructing the biological and sedimentological background of the formation of these stromatolites. Of particular importance is the question of whether the stromatolitic communities were dominated by photosynthetic microorganisms. The occurrence of phosphatic stromatolites in the internal voids of macrofossils buried in sediment, as well as within deep neptunian dykes or cavities in the rock substratum, may suggest that at least some of these communities were dependent on an energy source other than light. The microbial traces preserved in the stromatolites do not provide adequate information on the type of microorganisms involved in their formation, although a dominant role of bacteria has been postulated (Krajewski 1981a, 1983). On the other hand, the trapping and binding of detrital particles, as an important growth mechanism for some of the stromatolites covering hardgrounds or rockgrounds, implies a dense mat community dominated by filamentous miroorganisms, most probably cyanobacteria. Traces of filamentous meshworks have been noted in these stromatolites (e. g. Vera & Martín-Algarra, in press), though their poor preservation does not allow a more precise identification.

Another important problem of stromatolite development concerns the mechanism of phosphate precipitation within the microbial mats. Late Mesozoic stromatolites correspond to very low net accretion rates, which is indicated by the presence of nannofossils
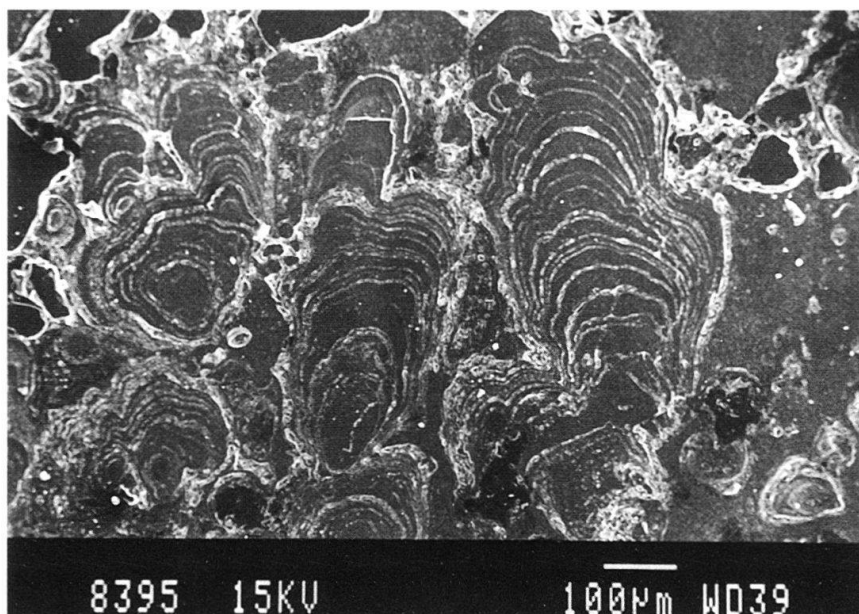
Fig. 18. Phosphatic microstromatolitic units composing a columnar stromatolite that developed at the top of highly condensed Turonian sediments in Zabierzów (S Poland). The microstromatolites show a delicate lamination made by the alternating compact (dark gray) and porous apatitic laminae (white to pale gray). The latter laminae contain common remnants of unicellular microorganisms, probably bacteria. The microstromatolitic fabric is typical for many Late Mesozoic phosphatic stromatolites formed as a result of phosphatization of microbial communites in submarine hiatal environments. SEM photomicrograph of polished stromatolite surface. Photo by K.P. Krajewski.

of different biostratigraphical zones within successive stromatolitic laminations (A. Martín-Algarra, unpublished data). On the other hand, the apatite making up the laminae exhibits ultrastructures typical of rapid mineral formation via metastable phosphate precursors (Fig. 19). The explanation of this apparent contradiction may require episodic apatite precipitation within the stromatolite-building microbial communities, implying recurrent pulses of phosphorus supply to a starved and relatively deep-water bottom environment. The mechanism is consistent with eutrophication events in the pelagic realm overlying the drowned carbonate platforms, suggested by the carbon isotopic record of the condensed stromatolite-bearing sequences (Funk et al. 1993; Föllmi et al. 1994; see also Glenn et al. 1994). An elevated content of severely degraded vertebrate remains (mostly debris of fish tooth enamel) in sediments directly associated with the phosphatic stromatolites in consistent with this interpretation. Systematic geomicrobiological investigations of the stromatolites combined with detailed isotopic studies of the stromatolitic apatite and the host sediment should provide a better insight into ancient biological processes involved in the formation of these unusual apatitic deposits.

## Concluding Remarks

The formation of authigenic marine apatite requires the presence, at sufficient levels, of the dissolved ionic species that participate in the precipitation reaction. Because of its extremely low concentrations in seawater, dissolved phosphate must, therefore, be generated in the pore water environment. The concentrations of dissolved phosphate in interstitial
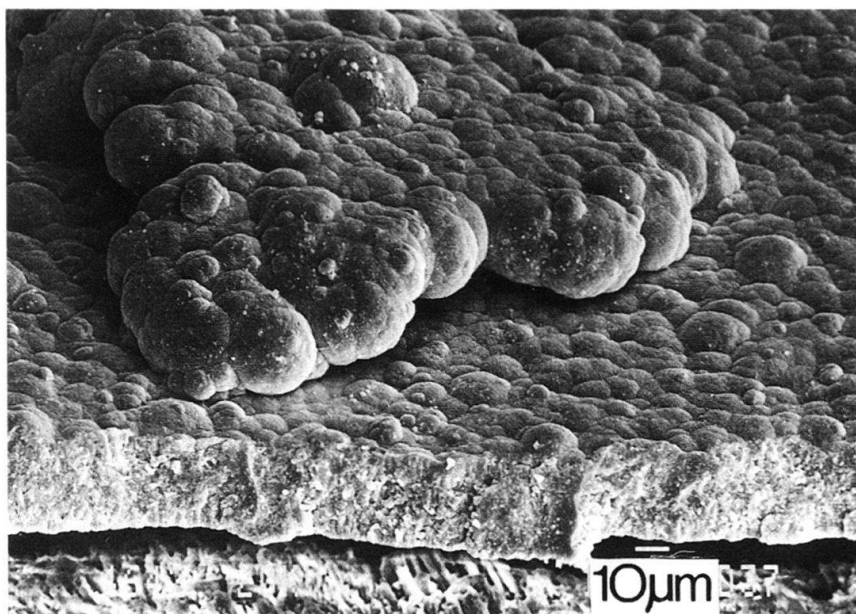
Fig. 19. Globular ultrastructure of apatite composing laminae in the Turonian phosphatic stromatolite in Zabierzów (S Poland). The morphology and spatial organization of the apatitic fabric suggest a rapid formation of a poorly ordered (or amorphous) phosphate phase involving a large number of nucleation sites in the microbial mat microenvironment (see also Fig. 18). Recurrent events of rapid phosphate emplacement within the microbial mat resulted in an upward growth of the laminated stromatolitic structure. SEM photomicrograph. Photo by K.P. Krajewski.

waters of coastal and shelf sediments frequently are observed to maintain significant degrees of supersaturation with respect to apatite. This means that the precipitation of apatite is possible in a range of continental margin depositional environments. However, the widespread disequilibrium in surficial sediments of these environments indicates that the precipitation of apatite is controlled by kinetic factors. Two different reaction pathways, characterized by different precipitation kinetics, lead to apatite deposition in sediments (Van Cappellen 1991). Precipitation may either result in a slow formation of apatite dispersed throughout the sediment, or in the rapid and episodic formation of phosphatic bodies. Precipitation experiments suggest that dispersed authigenic apatite is the result of the direct nucleation of apatite crystals, a kinetically very inefficient process. Individual phosphorite bodies on the other hand are explained by the initial, localized precipitation of a metastable precursor, creating a large number of crystallization sites. The precursor is replaced by apatite over time. The occurrence of one or the other mechanism of apatite formation is determined by the local levels of supersaturation attained in the surface sediments.

The mechanistic understanding of the basic nucleation and growth processes that are involved in the formation of authigenic apatite provides a framework in which to analyze the specific levels of microbial control of the precipitation process. Microbial activity modulates the average distribution of pore water dissolved phosphate, through its role in remobilizing particulate phosphorus fractions deposited from the water column. Sedimentary microorganisms drive the degradation of P-containing organic compounds and the reductive dissolution of P-sorbing ferric (hydr)oxides; they also accelerate the dissolution of skeletal phosphate debris. The transformation of particulate phosphorus into re-

active dissolved phosphate is presently the only unambiguous level at which microbial mediation is clearly driving apatite precipitation in sediments.

It is proposed here that in depositional environments characterized by a high supply of remobilizable particulate phosphorus, low detrital sedimentation and oxygen poor bottom waters, benthic microorganisms may provide an additional control on apatite formation. It is envisioned that dense microbial communities (e. g. mats) living at the water-sediment interface may efficiently fix the phosphate remobilized over the entire lenght of the surficial sediment into a fairly thin (dys)oxic surface layer. Redox fluctuations or burial of the microorganisms into the anoxic sediment may then result in a localized release of cellular phosphate to the pore water environment and induce the fast nucleation of a metastable calcium phosphate phase in proximity to the water-sediment interface. Rapid precipitation may lead to the phosphatization of microorganisms and macromolecular remains of their disintegration. There is, however, no convincing evidence that microbial membranes are indispensable for the nucleation of calcium phosphate phases.

A close association of benthic microbial activity and the formation of authigenic apatite can be widely traced in ancient marine phosphorites and phosphate-rich rock sequences. The basic lines of evidence are derived from the composition of organic matter preserved in phosphorites and from the mineral microstructures and fabrics of the phosphorites. The organic matter of phosphorites preserves a clear molecular signature of the intense early diagenetic degradation of sedimentary organic matter. Resistant humic substances resulting from the oxidative microbial degradation of organic matter are noted as a typical component in Phanerozoic phosphorites. The representation and distribution of biomarker compounds provides additional information on the type and intensity of microbial alterations of organic matter in phosphogenic sediments.

The mineral fabrics and ultrastructures of phosphorites provide an insight into the original distribution, arrangement and type of benthic microbiota. The large number of microbial fabrics in the mineral matrices of phosphorites is a witness of the abundance and diversity of bethic microbial life associated with fossil phosphogenic environments. Both the primary benthic producers and decomposing communities can be identified on the basis of detailed ultrastructure analysis. The extracellular precipitation of apatite was a common mechanism of microbiota preservation, although fossilized remnants of the original organic structures are sometimes found in phosphorites. The ultrastructure and spatial organization of the microbial phosphatic fabrics do not seem to support earlier hypotheses of a direct cellular control of apatite precipitation in ancient phosphogenic environments. The localized development of phosphatic bodies composing many ancient phosphorites is, however, likely to reflect spatial controls of apatite precipitation exerted by the activity of entire benthic microbial communities. Stromatolitic phosphorites provide an extreme example of a strict spatial association between the activities of dense microbial mats and the precipitation and concentration of apatite.

## Acknowledgements

## REFERENCES

ADDADI, L. & WEINER, S. 1985: Interactions between acidic proteins and crytals: Stereochemical requirements in biomineralization. Proc. Nat. Acad Sci. U.S.A. 82, 4110–4114.

AL-BASSAM, K.S. 1989: The Akhashat phosphate deposit, Iraq. In: Phosphate Deposits of the World. Vol. 2. Phosphate Rock Resources (Ed. by A.J.G. NOTHOLT, R.P. SHELDON & D.F. DAVIDSON). Cambridge Univ. Press, Cambridge, 316–322.

AMIT, O. & BEIN, A. 1982: Organic matter in Senonian phosphorites from Israel: Origin and diagenesis. Chem. Geol. 37, 277–287.

ARTHUR, M.A., DEAN, W.E., ZACHOS, J.C., KAMINSKI, M., HAGERTY RIEG, S. & ELSTROM, K. 1985: Geochemical expression of early diagenesis in Middle Eocene – Lower Oligocene pelagic sediments in the southern Labrador Sea, Site 647. Proc. Ocean Dril. Project, Sci. Results 105, 111–136.

ATFEH, S. 1989: The phosphorite resources of Syria. In: Phosphate Deposits of the World. Vol. 2. Phosphate Rock Resources (Ed. by A.J.G. NOTHOLT, R.P. SHELDON & D.F. DAVIDSON). Cambridge Univ. Press, Cambridge, 357–362.

AWRAMIK, S.M. 1971: Precambrian columnar stromatolite diversity: Reflection of metazoan appearance. Science 174, 825–827.

– 1984: Ancient stromatolites and microbial mats. In: Microbial Mats: Stromatolites (Ed. by Y. COHEN, R.W. CASTENHOLZ & H.O. HALVORSON). MBL Lectures in Biology 3. Alan R. Liss, Inc. New York, 1–22.

AWRAMIK, S.M., MARGULIS, L. & BARGHOON, E.S. 1976: Evolutionary processes in the formation of stromatolites. In: Stromatolites (Ed. by M.R. WALTER). Developments in Sedimentology 20. Elsevier, Amsterdam, 149–191.

BAKER, P. & ALLEN, M. 1990: Occurrence of dolomite in Neogene phosphatic sediments. In: Phosphate Deposits of the World. Vol. 3. Neogene to Modern Phosphorites (Ed. by W.C. BURNETT & S.R. RIGGS). Cambridge Univ. Press, Cambridge, 75–86.

BANERJEE, D.M. 1971: Precambrian stromatolitic phosphorite of Udaipur, Rajasthan, India. Geol. Soc. Am. Bull. 82, 2319–2330.

BANERJEE, D.M., BASU, P.C. & SRIVASTAVA, N. 1980: Petrology, mineralogy, geochemistry and origin of the Precambrian Aravallian phosphorite deposits of Udaipur and Jhabua, India. Econ. Geol. 75, 1181–1199.

BANERJEE, D.M., SCHIDLOWSKI, M. & ARNETH, J.D. 1986: Genesis of Upper Proterozoic-Cambrian phosphorite deposits of India: Isotope inferences from carbonate fluorapatite, carbonate and organic carbon. Precambrian Res. 33, 239–253.

BATURIN, G.N. 1982: Phosphorites on the Sea Floor. Origin, Composition and Distribution. Developments in Sedimentology 33. Elsevier, Amsterdam.

– 1983: Some unique sedimentological and geochemical features of deposits in coastal upwelling regions. In: Coastal Upwelling, Its Sediment Record. Part B: Sedimentary Record of Ancient Coastal Upwelling (Ed. by J. THIEDE & E. SUESS). Plenum Press, New York, 11–27.

BATURIN, G.N. & DUBINCHUK, V.T. 1979: Microstructures of Oceanic Phosphorites. Atlas of Photomicrographs. Izd. Nauka, Moscow (in Russian).

BATURIN, G.N., BERSENEV, I.I., GUSEV, V.V., LELIUKOV, E.P., SCHEVCHENKO, A.J. & SHKOLNIK, E.L. 1985: Ultramicroscopic investigation of the structure of phosphorites from the bottom of the Sea of Japan. Dokl. Akad. Nauk SSSR 281, 1169–1172 (in Russian).

BEIN, A. & AMIT, O. 1982: Depositional environments of the Senonian chert, phosphorite and oil shale sequence in Israel as deduced from their organic matter composition. Sedimentology 29, 81–90.

BELAYOUNI, H. 1983: Étude de la Matière Organique dans la Série Phosphatée du Bassin de Gafsa-Metlaoui, Tunisie. Application à la Compréhension des Mécanismes de la Phosphatogenèse. Ph. D. Thesis. Université d'Orléans, Orléans.

BELAYOUNI, H. & TRICHET, J. 1980a: Contribution à la connaissance de la matière organique du bassin phosphaté de Gafsa: Informations fournies par l'analyse du potentiel pétrolier. In: Géologie Comparée des Gisements de Phosphates et de Pétrole (Ed. by J. BODELLE, A. PERRODON, M. SLANSKY & H. RADIER). Doc. BRGM 24, 37–59.

– 1980b: Glucosamine as a biochemical marker for dinoflagellates in phosphate sediments. In: Advances in Organic Geochemistry 1979 (Ed. by A.G. DOUGLAS & J.R. MAXWELL). Pergamon Press, Oxford, 205–210.

– 1984: Hydrocarbons in phosphatized and non-phosphatized sediments from the phosphate basin of Gafsa (Tunisia). Org. Geochem. 6, 741–754.

BELAYOUNI, H., SLANSKY, M. & TRICHET, J. 1990: A study of the organic matter in Tunisian phosphate-bearing series (Gafsa Basin, Tunisia). Relevance to phosphorite genesis. Org. Geochem. 15, 47–72.

BENALIOULHAJ, S. 1989: Géochimie Organique de la Série Phosphatée du Basin des Ouldad-Abdoun et de la Série Bitumineuse du Bassin de Timahdit (Crétacé Superieur-Eocène, Maroc). Ph. D. Thesis. Université d'Orléans, Orléans.

BENALIOULHAJ, S. & TRICHET, J. 1990: Camparative study by infrared spectroscopy of the organic matter of phosphate-rich (Ouldad Abdoun basin) and black shale (Timahdit basin) series (Morocco). Org. Geochem. 16, 649–660.

BERKER, E. 1989: The Mardin-Mazidagi-Derik phosphate deposit, south east Turkey. In: Phosphate Deposits of the World. Vol. 2. Phosphate Rock Resources (Ed. by A.J.G. NOTHOLT, R.P. SHELDON & D.F. DAVIDSON). Cambridge Univ. Press, Cambridge, 380–386.

BERNER, R.A. 1982: Burial of organic carbon and pyrite sulfur in the modern ocean: Its geochemical and environmental significance. Am. J. Sci. 282, 451–473.

BERNER, R.A., RUTTENBERG, K.C., INGALL, E.D. & RAO, J.-L. 1993: The nature of phosphorus burial in modern marine sediments. In: Interactions of C, N, P and S Biogeochemical Cycles and Global Change (Ed. by R. WOLLAST, F.T. MACKENZIE & L. CHOU). Springer-Verlag, Berlin, 365–378.

BODELLE, J., PERRODON, A., SLANSKY, M. & RADIER, H. (Eds) 1980: Géologie Comparée des Gisements de Phosphates et de Pétrole. Colloq. Int. Orléans 6–7 nov. 1979. Doc. BRGM 24.

BOSTRÖM, K. & BACKMANN, J. 1990: Geochemistry and origin of Neogene sediments in Hole 711A. Proc. Ocean Dril. Project. Sci. Results 115, 699–708.

BOSTRÖM, K., JOENSUN, O., VALDÉS, S., CHARM, W. & GLACCUM, R. 1976: Geochemistry and origin of East Pacific sediments sampled during DSDP Leg 34. Initial Reports DSDP 34, 559–574.

BRÉHÉRET, J.-G. 1991: Phosphatic concretions in black facies of the Aptian-Albian Marnes bleues Formation of the Vocontian basin (SE France), and at site DSDP 369: Evidence of benthic microbial activity. Cretaceous Res. 12, 411–435.

BREMNER, J.M. 1980: Concretionary phosphorite from SW Africa. J. geol. Soc. London 137, 773–786.

BROECKER, W.S. & PENG, T.H. 1982: Traces in the Sea. Eldigrio Press.

BRUMSACK, H.J. 1991: Inorganic geochemistry of the German "Posidonia Shale": Paleoenvironmental consequences. In: Modern and Ancient Continental Anoxia (Ed by R.V. TYSON & T.H. PEARSON). Geol. Soc. Spec. Publ. No. 58, 353–362.

BURDIGE, D.J. & NELSON, K.H. 1986: Chemical and microbiological studies of sulfide-mediated manganese reduction. Geomicrobiol. J. 4, 361–387.

BUSHINSKI, G.I. 1964: On shallow water origin of phosphorite sediments. In: Deltaic and Shallow Water Sediments (Ed. by L.M.J.U. VAN STRAATEN). Developments in Sedimentology 1. Elsevier, Amsterdam, 62–70.

– 1969: Old Phosphorites of Asia and their Genesis. Izd. Nauka, Moscow (in Russian).

CARLTON, R.G. & WETZEL, R.G. 1988: Phosphorus flux from lake sediments: Affect of epipelic algal oxygen production. Limnol. Oceanogr. 33, 562–570.

CAYEUX, L. 1936: Existence de nombreuses Bactéries dans les phosphates sédimentaires de tout âge. Conséquences. C. R. Acad. Sc. Paris 203, 1198–1200.

CHAMLEY, H. & DEBRABANT, P. 1984: Mineralogical and geochemical investigations of sediments of the Mazagan Plateau, Northwestern African Margin, Leg 79, Deep Sea Drilling Project. Initial Reports DSDP 79, 497–508.

CHAUHAN, D.S. 1979: Phosphorite bearing stromatolites of the Precambrian Aravalli phosphorite deposits of Udaipur region, their environmental significance and genesis of phosphorite. Precambrian Res. 8, 95–126.

– 1980: Stromatolites of Nimach Mata and Beragaon phosphorite deposits and genesis of rock phosphate. Geol. Surv. India Misc. Publ. 44, 314–329.

CHAUHAN, D.S. & SISODIA, M.S. 1981: Nature of Udaipur phosphorite and the genetic implication. Proc. 4th Int. Field Semin. Phosphorite, India.

COHEN, Y. & ROSENBERG, E. (Eds.) 1989: Microbial Mats. Physiological Ecology of Benthic Microbial Commu-
    nities. Amer. Soc. Microbiol. Washington.
COHEN, Y., CASTENHOLZ, R.W. & HALVORSON, H.O. (Eds.) 1984: Microbial Mats: Stromatolites. MBL Lec-
    tures in Biology 3. Alan R. Liss, Inc. New York.
COOK, P.J. & SHERGOLD, J.H. 1986: Proterozoic and Cambrian phosphorites – nature and origin. In: Phosphate
    Deposits of the World. Vol. 1. Proterozoic and Cambrian Phosphorites (Ed. by P.J. COOK & J. H. SHER-
    GOLD). Cambridge Univ. Press, Cambridge, 369–386.
CORBRIDGE, D.E.C. 1985: Phosphorus. An Outline of its Chemistry, Biochemistry and Technology. Studies in
    Inorganic Chemistry 6. Elsevier, Amsterdam.
CROWLEY, S.T., STOW, D.A.V., BOUQUILLION, A. & TIERCELIN, J.-J. 1990: Major element geochemistry and clay
    mineralogy and their relationship to facies discrimination in distal Bengal Fan Sediments, Leg 116. Proc.
    Ocean Dril. Project 116 (Sci. Results, back pocket microfiche).
CUNNINGHAM, R. & KROOPNICK, R.M. 1981: Inorganic and isotopic geochemistry of sediments from Sites 549
    and 551, North Eastern North Atlantic. Initial Reports DSDP 80, Part 2, 1073–1079.
DAHANAYAKE, K. & KRUMBEIN, W.E. 1985: Ultrastructure of a microbial-mat generated phosphorite. Mineral.
    Deposita 20, 260–265.
DEAN, W.E., ARTHUR, M.A. & STOW, D.A.V. 1984: Origin and geochemistry of Cretaceous black shales and
    multicolored claystones, with emphasis on Deep Sea Drilling Project Site 530, Southern Angola Basin. In-
    itial Reports DSDP 75, Part 2, 819–844.
DELAMETTE, M. 1981: Sur la découverte de stromatolites circalittoraux dans le partie moyenne du Crétacé
    nord-subalpin (Alpes occidentales, françaises). C.R. Acad. Sc. Paris 292, Sér. II, 761–764.
–       1986: L'Évolution du Domaine Helvétique, Entre Bauges et Morcles, de l'Aptien Supérieur au Turonien:
    Séries Condensées, Phoshorites et Circulations Océaniques (Alpes Occidentales, Franco-Suisses). Ph. D.
    Thesis. Univ. Genève, No. 2237.
EGANOV, E.A. 1988: Phosphate Deposition and Stromatolites. Inst. Geol. & Geophys. Akad Nauk SSSR, No-
    vosibirsk (in Russian).
EL FALEH, E.M. 1988: Les Méchanismes de Synthèse de l'Apatite par Activité Bactérienne. Rôle et Comporte-
    ment de quelques Éléments Minéraux. Application aux Phosphates Sédimentaires. Ph. D. Thesis,
    Université Louis Pasteur, Strasbourg.
ELIOTT, J.C. 1985: Controlled crystallization. Nature 317, 387–388.
EMELYANOV, E.M. & TRIMONIS, E.S. 1983: Geochemical investigations of sediment from the Brasil Basin and
    the Rio Grande Rise. Initial Reports DSDP 72, 421–427.
EMELYANOV, E.M., LISITZIN, A.P., SHIMKUS, K.M., TRIMONIS, E.S., LUKASHEV, V.K., LUKASHIN, V.N., MITRO-
    POLSKIY, A.YU. & PILIPCHUK, M.F. 1978: Geochemistry of Late Cenozoic sediments of the Black Sea, Leg
    42B. Initial Reports DSDP 42, 543–605.
FIKRI, A. 1991: Contribution à l'Etude le la Géochimie Organique des phosphates insulaires. Implication dans
    la Phosphatogenèse. Ph. D. Thesis. Unviersité d'Orléans, Orléans.
FILIPELLI, G.M. & DELANEY, M.L. 1993a: Phosphogenesis and the control on phosphorus accumulation in con-
    tinental magin sediments. In: Siliceous, Phosphatic and Glauconitic Sediments (Ed. by A. IIYNA & R.E.
    GARRISON). Int. Geol. Congr. Proc. 29.
–       1993b: Phosphorus geochemistry and accumulation rates in the Eastern Equatorial Pacific Ocean: Results
    from Leg 138. Proc. Ocean Dril. Project, Sci Results 138 (in press).
FÖLLMI, K.B. 1989: Evolution of the Mid-Cretaceous triad: platform carbonates, phosphatic sediments, and
    pelagic carbonates along the northern Tethys margin. Lecture Notes in Earth Sciences 23. Springer-Verlag,
    Berlin.
–       1990: Condensation and phosphogenesis: Example from the Helvetic mid-Cretaceous (northern Tethyan
    margin). In: Phosphorite Research and Development (Ed. by A.J.G. NOTHOLT & I. JARVIS). Geol. Soc.
    Spec. Publ. London No. 52, 237–252.
FÖLLMI, K.B. & GARRISON, R.E. 1991: Phosphatic sediments, ordinary or extraordinary deposits? The example
    of the Miocene Monterey Formation (California). In: Controversies in Modern Geology (Ed. by
    D. MÜLLER, J.A. MACKENZIE & H. WEISSERT). Academic Press, London 55–84.
FÖLLMI, K.B. & OUWEHAND, P.J. 1987: Garschella-Formation und Götzis-Schichten (Aptian-Coniacian): Neue
    stratigraphische Daten aus dem Helvetikum der Ostschweiz und des Vorarlbergs. Eclogae geol. Helv. 80,
    141–191.
FÖLLMI, K.B. & WEISSERT, H., BISPING, M. & FUNK, H. 1994: Phosphogenesis, carbon-isotope stratigraphy, and
    carbonate-platform evolution along the Lower Cretaceous northern Tethyan margin. Geol. Soc. Am Bull.
    106, 729–746.

FRECHE, M. & LACOUT, J.L. 1992: Effect of humic compounds and some organic acids added during dicalcium phosphate dihydrate crystal growth process. J. Alloys Compounds 188, 65–68.

FROELICH, P.N., BENDER, M.L., LUEDTKE, N.A., HEATH, G.R. & DEVRIES, T. 1982: The marine phosphorus cycle. Am. J. Sci. 282, 474–511.

FROELICH, P.N., & ARTHUR, M.A., BURNETT, W.C., DEAKIN, M., HENSLEY, V., JAHNKE, R., KAUL, L., KIM, K.-H., ROE, K., SOUTAR, A. & VATHAKANON, C. 1988: Early diagenesis of organic matter in Peru continental margin sediments: Phosphorite precipitation. Mar. Geol. 80, 309–343.

FUNK, H., FÖLLMI, K.B. & MOHR, H. 1993: Evolution of the Tithonian – Aptian carbonate platform along the northern Tethyan margin, eastern Helvetic Alps. In: Cretaceous Carbonate Platforms (Ed. by T. SIMO, R.W. SCOTT & J.P. MASSE). Am Assoc. Petroleum Geol. Mem. 56, 387–407.

GÄCHTER, R., MEYER, J.S. & MARES, A. 1988: Contribution of bacteria to release and fixation of phosphorus in lake sediments. Limnol. Oceanogr. 33, 1542–1558.

GALLARDO, V.A. 1977: Large benthic microbial communities in sulphide biota under Peru-Chile Subsurface Countercurrent. Nature 268, 331–332.

GARRISON, R.E. & KASTNER, M. 1990: Phosphatic sediments and rocks recovered from the Peru margin during ODP Leg 112. In: Proceedings of the Ocean Drilling Program, Scientific Results (Ed. by E. SUESS, R. VAN HUENE et al.) Vol. 112, 111–134.

GARRISON, R.E., KASTNER, M. & KOLODNY, Y. 1987: Phosphorites and phosphatic rocks in the Monterey Formation and related Miocene units, coastal California. In: Cenozoic Basin Development of Coastal California (Ed. by R.V. INGERSOLL & W.G. ERNST). Prentics-Hall Inc., New Jersey, 348–381.

GASSMANN, G. 1982: Detection of aliphatic hydrocarbons derived by recent "bio-conversion" from fossil fuel oil in North Sea waters. Mar. Poll. Bull. 13, 309–315.

GHOSH, K. & SCHNITZER, M. 1980: Macromolecular structures of humic substances. Soil Sci. 129, 266–276.

GLENN, C.R. & ARTHUR, M.A. 1988: Petrology and major element geochemistry of Peru margin phosphorites and associated diagenetic minerals: Authigenesis in modern organic-rich sediments. Mar. Geol. 80, 231–276.

– 1990: Anatomy and origin of a Cretaceous phosphorite-greensand giant, Egypt. Sedimentology 37, 123–154.

GLENN, C.R., ARTHUR, M.A., YEH, H.-W. & BURNETT, W.C. 1988: Carbon isotopic composition and lattice-bound carbonate of Peru-Chile margin phosphorites. Mar. Geol. 80, 287–307.

GLENN, C.R., FÖLLMI, K.B., RIGGS, S.R. BATURIN, G.N., GRIMM, K.A., TRAPPE, J., ABED, A.M., GALLI-OLIVIER, C., GARRISON, R.E., ILYIN, A., JEHL, C., ROHLICH, V., SADAQUAH, R., SCHIDLOWSKI, M., SHELDON, R.E. & SIEGMUND, H. 1994: Phosphorus and phosphorites: Sedimentology and environments of formation. Eclogae geol. Helv. 87, 747–788.

GOLDHABER, M.B., ALLER, R.,C., COCHRAN, J.K., ROSENFIELD, J.K., MARTENS, C.S. & BERNER, R.A. 1977: Sulfate reduction, diffusion and bioturbation in Long Island Sound sediments: Report of the FOAM group. Am. J. Sci. 277, 193–273.

GOLONKA, R. & RAJCHEL, R. 1972: Upper Cretaceous stromatolites in the vicinity of Cracow. Kwart. geol. 22, 515–538.

GULBRANDSEN, R.A., ROBERSON, C.E. & NEIL, S.T. 1984: Time and crystallization of apatite in seawater. Geochim. Cosmochim. Acta 48, 213–218.

HALDIMANN, P.A. 1977: Sedimentologische Entwicklung der Schichten an einer Zyklengrenze der Helvetischen Unterkreide; Pygurus-Schichten und Gemsmättli-Schicht (Valanginian/Hauterivian) zwischen Thunersee und St. Galler Rheintal. Diss. ETH Zürich.

HARLAND, W.B., ARMSTRONG, R.L., COX, A.V., CRAIG, L.E., SMITH, A.G. & SMITH, D.G. 1989: A Geological Time Scale. Cambridge Univ. Press, Cambridge.

HEATH, J.R., KOVAR, R.B. & LOPEZ, C. 1986a: Geochemistry of Sites 579, 580 and 581 Deep Sea Drilling Project, Leg 86, Western North Pacific. Initial Reports DSDP 86, 657–670.

HEATH, J.R., KOVAR, R.B., LOPEZ, C. & CAMPI, G.L. 1986b: Elemental composition of Cenozoic pelagic clays from Deep Sea Drilling Project, Sites 579, 580 and 581 Deep Sea Drilling Project, Leg 86, Western North Pacific. Initial Reports DSDP 86, 605–646.

HENRICHS, S.M. & FARRINGTON, J.W. 1984: Peru upwelling region sediments near 15°S. Remineralization and accumulation of organic matter. Limnol. Oceanogr. 29, 1–19.

HIRSCHLER, A. 1990: Étude de l'Intervention des Microorganismes dans la Formation de l'Apatite. Ph. D. Thesis, Université Louis Pasteur, Strasbourg.

HIRSCHLER, A., LUCAS, J. & HUBERT, J.-G. 1990a: Apatite genesis: A biologically induced or biologically controlled mineral formation process? Geomicrobiol. J. 7, 47–57.

–   1990b: Bacterial involvement in apatite genesis. FEMS Microbiol. Ecol. 73, 211–220.

HOLLAND, H.D. 1978: The Chemistry of the Atmosphere and the Oceans. Wiley-Interscience.

INGALL, E.D., SCHROEDER, P.A. & BERNER, R.A. 1990: The nature of organic phosphorus in marine sediments: New insights from $^{31}$P NMR. Geochim. Cosmochim. Acta 54, 2617–2620.

INGALL, E.D., BUSTIN, R.M. & VAN CAPPELLEN, P. 1993: Influence of water column anoxia on the burial and preservation of carbon and phosphorus in marine shales. Geochim. Cosmochim. Acta 57, 303–316.

INSKEEP, W.P. & SILVERTOOTH, J.C. 1989: Inhibition of hydroxyapatite precipitation in the presence of fulvic, humic and tannic acids. Soil Sci. Soc. Am. J. 52, 941–946.

JAHNKE, R.A. 1984: The synthesis and solubility of carbonate fluorapatite. Am. J. Sci. 284, 58–78.

JAHNKE, R.A., EMERSON, S.R., ROE, K.K. & BURNETT, W.C. 1983: The present day formation of apatite in mexican continental margin sediments. Geochim. Cosmochim. Acta 47, 259–266.

JARRARD, R.D. & LYLE, M. 1991: High resolution geochemical variations at Sites 723, 728 and 731: A comparison of X-ray fluorescence and geochemical logs. Proc. Ocean Dril. Project, Sci. Results 117, 473–498.

JARVIS, I. 1985: Geochemistry and origin of Eocene-Oligocene metalliferous sediments from the Equatorial Pacific deep sea. Deep Sea Drilling Project Sites 573 and 574. Initial Reports DSDP 85, 781–804.

JARVIS, I., BURNETT, W.C., NATHAN, Y., ALMBAYDIN, F.S.M., ATTIA, A.K.M., CASTRO, L.N., FLICOTEAUX, R., HILMY, M.E., HUSAIN, V., QUTAWNAH, A.A., SERJANI, A. & ZANIN, YU.N. 1994: Phosphorite geochemistry: State-of-the-art and environmental concerns. Eclogae geol. Helv. 87, 643–700.

JENKYNS, H.C. 1980: Cretaceous anoxic events: From continents to oceans. Jour. geol. Soc. London 137, 171–188.

JÖRGENSEN, B.B. 1982: Ecology of the bacteria of the sulphur cycle with special reference to anoxic-oxic interface environments. Phil. Trans. R. Soc. London B298, 543–561.

JÖRGENSEN, B.B. & REVSBECH, N.P. 1983: Colorless sulfur bacteria, *Beggiatoa* spp. and *Thiovulum* spp., in $O_2$ and $H_2S$ microgradients. App. Environ. Microbiol. 45, 1261–1270.

KIM, K.-H. & BURNETT, W.C. 1986: Uranium-series growth history of a Quaternary phosphatic crust from the Peruvian continental margin. Chem. Geol. 58, 227–244.

KNAUER, G.A., MARTIN, J.H. & BRULAND, K.W. 1979: Fluxes of particulate carbon, nitrogen and phosphorus in the upper water column of the northeast Pacific. Deep-Sea Res. 26, 97–108.

KRAJEWSKI, K.P. 1981a: Phosphate microstromatolites in the High-Tatric Albian limestones in the Polish Tatra Mountains. Bull. Acad. Pol. Sci. Ser. Sci. Terre 29, 175–183.

–   1981b: Pelagic stromatolites from the High-Tatric Albian limestones in the Tatra Mts. Kwart. geol. 25, 731–759.

–   1983: Albian pelagic phosphate-rich macrooncoids from the Tatra Mts., Poland. In: Coated Grains (Ed. by T.M. PERYT). Springer-Verlag, Berlin, 344–357.

–   1984: Early diagenetic phosphate cements in the Albian condensed glauconitic limestone of the Tatra Mountains, Western Carpathians. Sedimentology 31, 443–470.

–   1989: Organic geochemistry of a phosphorite to black shale transgressive succession: Wilhelmöya and Janusfjellet Formations (Rhaetian-Jurassic) in central Spitsbergen. Chem. Geol. 74, 249–263.

KRASILNIKOVA, N.A. & PAUL, R.K. 1983: Stromatolitic phosphorites of Gornaya Shoriya. Geol. & Geophys. 24, 56–61.

KUMAR, S. & MULLER, G. 1988: Geochemistry, mineralogy and genesis of phosphatic stromatolites. Gangolihat Dolomite (Riphean), Kumaun Himalaya, India. Heidelberger Geowiss. Abh. 20, 87–136.

KURNOSOV, V.B. & CHUDAEV, O.V. 1983: Mineralogy and geochemistry of sediments from Galapagos hydrothermal mounts, Leg 70, Deep Sea Drilling Project. Initial Reports DSDP 70, 225–233.

KURNOSOV, V.B., MURKNAA, I.A., KAZAKOVA, V., SCHEVCHENKO, A. & SHIRSHOV, P.P. 1983: Mineralogy and inorganic geochemistry of sediments from the mouth of the Gulf of California. Initial Reports DSDP 65, 399–424.

LAMBOY, M. 1990a: Microbial mediation in phosphatogenesis: new data from the Cretaceous phosphatic chalks of northern France. In: Phosphorite Research and Development (Ed. by A.J.G. NOTHOLT & I. JARVIS). Geol. Soc. Spec. Publ. London No. 52, 157–167.

–   1990b: Microstructures of a phosphatic crust from the Peruvian continental margin: Phosphatized bacteria and associated phenomena. Oceanol. Acta 13, 439–451.

–   1993: Phosphatization of calcium carbonate in phosphorites: Microstructure and importance. Sedimentology 40, 53–62.

–   1994: Nannostructure and genesis of phosphorites from ODP Leg 112, the Peru margin. Mar. Geol. 118 (in press).

LAMBOY, M. & MONTY, C. 1987: Bacterial origin of phosphatized grains (Abstr.). Terra Cognita 7, 207.

LEGETT, J.K. 1982: Geochemistry of Cocos Plate pelagic-hemipelagic sediments in Hole 487, Deep Sea Drilling Project, Leg 66. Initial Reports DSDP 66, 683–686.

LEWY, Z. 1990: Pebbly phosphate and granular phosphorite (Late Cretaceous, southern Israel) and their bearing on phosphatization processes. In: Phosphorite Research and Development (Ed. by A.J.G. NOTHOLT & I. JARVIS). Geol. Soc. Spec. Publ. London No. 52, 169–178.

LISITZIN, A.P., SEROVA, V.V., ZVERNISKAYA, I.B., LUKASHIN, V., GORBUNOVA, Z.N., GORDEEV, V.V., ZHURENSKO, V.V., PCHELNITSEV, A.M., BELYAEV, YU.Y., POPOV, N.I., SHISKINA, O.V., MOTOZOY, N.M., JOUSE, A.P., KOZLOVA, O.G. MUKHINA, V.V., KHODKEVICH, YU.N. & PAYUSNINA, I.I. 1971: Geochemical, mineralogical and paleontological studies. Initial Report DSDP 6, 829–960.

LOUGHMAN, D.L. 1984: Phosphate authigenesis in the Aramachay Formation (Lower Jurassic) of Peru. Jour. Sediment. Petrol. 54, 1147–1156.

LOVLEY, D.R. & PHILLIPS, E.J.P. 1988: Novel mode of microbial energy metabolism: Organic carbon oxidation coupled to dissimilatory reduction of iron and manganese. Appl. Environ. Microbiol. 54, 1472–1480.

LUCAS, J. & PRÉVÔT, L. 1981: Synthèse d'apatite à partir de matière organique phosphorée (ARN) et de calcite par voie bactérienne. C. R. Acad Sc. Paris II 292, 1203–1208.

– 1984: Synthèse de l'apatite par voie bactérienne à partir de matière organique et de divers carbonates de calcium dans des eaux douce et marine naturelles. Chem. Geol. 42, 101–118.

– 1985: The synthesis of apatite by bacterial activity: Mechanism. Sci. Géol. Mém. Strasbourg 77, 83–92.

LYLE, M.W. 1983: Major element composition of Leg 92 sediments. Initial Reports DSDP 92, 355–370.

MANN, S. 1989: Crystallochemical strategies in biomineralization. In: Biomineralization – Chemical and Biochemical Perspectives (Ed. by S. MANN, J. WEBB & R.J.P. WILLIAMS). VCH Verlag, Weinheim, 35–62.

MARCINOWSKI, R. 1974: The transgressive Cretaceous (Albian through Turonian) deposits of the Polish Jura Chain. Acta Geol. Pol. 24, 117–217.

MARCINOWSKI, R. & SZULCZEWSKI, M. 1972: Condensed Cretaceous sequence with stromatolites in the Polish Jura Chain. Acta Geol. Pol. 22, 515–538.

MARTIN-ALGARRA, A. & VERA, J.A.: Mesozoic pelagic stromatolites from the Penibetic (Betic Cordillera, Southern Spain). In: Phanerozoic Stromatolites II (Ed. by C. MONTY & J. SARFATI). Kluwer Acad. Press. (in press).

MASLOV. V.P. 1960: Stromatolites. Trudy Geol. Inst. Akad. Nauk SSSR 41 (in Russian).

MASSARI, F. & MEDIZZA, F. 1973: Stratigrafia e paleogeografia del Campaniano-Maastrichtiano nelle Alpi Meridionali (con particolare agli hardgrounds della Scaglia Rossa Veneta). Mem Ist. Geol. Univ. Padova 28.

MAUGHAN, E.K. 1980: Relation of phosphorite, organic carbon, and hydrocarbons in the Permian Phosphoria Formation, Western United States of America. In: Géologie Comparée des Gisements de Phosphates et de Pétrole (Ed. by J. BODELLE, A. PERRODON, M. SLANSKY & H. RADIER). Doc. BRGM 24, 63–91.

MCARTHUR, J. 1986: Stable isotopic characterization of francolite formation. Earth Planet. Sci. Lett. 77, 20–34.

MCLEAN, R.J.C. & BEVERIDGE, T.J. 1990: Metal-binding capacity of bacterial surfaces and their ability to form mineralized aggregates. In: Microbial Mineral Recovery (Ed. by H.L. EHRLICH & C.L. BRIERLY). McGraw-Hill, New York, 185–222.

MEUNIER-CHRISTMANN, C. 1988: Géochimie Organique de Phosphates et Schistes Bitumineux Marocains: Etude du Processus de Phosphatogenèse. Ph. D. Thesis. Université Louis Pasteur, Strasbourg.

MEUNIER-CHRISTMANN, C., LUCAS, J. & ALBRECHT, P. 1989: Organic geochemistry of Maroccan phosphorites and bituminous shales. A contribution to the problem of phosphogenesis. In: Apatite and Phosphorites (Ed. by P.J. COOK & L. PRÉVÔT). Sci. Géol. Bull. Strasbourg 42, 205–222.

MIGIDISOV, A.A., GRADUSOV, B.P., BREDANOVA, N.V., BEZROGOVA, E.V., SAVLIEV, B.V. & SMIRNOVA, O.N. 1983: Major and minor elements in hydrothermal and pelagic sediments of the Galapagos mounts area, Leg 70, Deep Sea Drilling Project. Initial Reports DSDP 70, 277–298.

MINAI, Y., MATSUMOTO, R. & TOMINAGA, T. 1986: Geochemistry of deep sea sediments from the Nankai trough, the Japan trench and adjacent regions. Initial Reports DSDP 87, 643–658.

MITROV, YU.V., ZANIN, YU.N., KRASILNIKOVA, N.A., GUREVICH, B.G., KRIVOPUTSKAYA, L.M., KRASILNIKOVA, I.G. & SUKHOV, YU.K.M. 1987: Ultramicrostructures of Phosphorites. Izd. Nauka, Moscow (in Russian).

MITTERER, R.M. & CUNNINGHAM, R. JR. 1985: The interaction of natural organic matter with grain surfaces: Implications for calcium carbonate precipitation. Soc. Econ. Paleontol. Min., Spec. Publ. 36, 17–31.

MONCIARDINI, C. 1989: The Senonian (Cretaceous) phosphatic chalks of the Paris Basin, France. In: Phosphate Deposits of the World. Vol. 2. Phosphate Rock resources (Ed. by A.J.G. NOTHOLT, R.P. SHELDON & D.F. DAVIDSON). Cambridge Univ. Press, Cambridge, 407–410.

MONTY, C.L.V. 1973: Precambrian background and Phanerozoic history of stromatolitic communities, An overview. Ann. Soc. Géol. Belg. 96, 585–624.

MULLINS, H.T. & RASCH, R.F. 1985: Sea-floor phosphorites along the central California continental margin. Econ. Geol. 80, 696–715.

MURRAY, R.W. & LEINEN, M. 1993: Chemical transport to the seafloor of the Equatorial Pacific Ocean across a latitudinal transect at 135° W: Tracking sedimentary, major, trace, and rare earth element fluxes at the equator and intertropical convergence zone. Geochim. Cosmochim. Acta 57, 4141–4163.

NATHAN, Y. 1990: Humic substances in phosphorites: Occurrence, characterization and significance. In: Phosphate Research and Development (Ed. by A.J.G. NOTHOLT & I. JARVIS). Geol. Soc. Spec. Publ. London No. 52, 49–58.

NELSON, D.C. & JANNASCH, H.W. 1983: Chemoautotrophic growth of marine Beggiatoa in sulphide-gradient cultures. Arch. Microbiol. 136, 262–269.

NELSON, D.C., REVSBECH, N.P. & JÖRGENSEN, B.B. 1986: Microoxic-anoxic niche of Beggiatoa spp.: Microelectrode survey of marine and freshwater strains. App. Environ. Microbiol. 52, 161–162.

NISSENBAUM, A. 1979: Phosphorus in marine and non marine humic substances. Geochim. Cosmochim. Acta 43, 1973–1978.

NRIAGU, J.O. 1983: Rapid decomposition of fish bones in Lake Erie sediments. Hydrobiologia 106, 217–222.

NTB 84–86 1984: Die Kernbohrung Beznau. Nagra Technischer Bericht NTB 84–86. Beitr. Geol. Schweiz. Geotechnische Serie 66.

O'BRIEN, G.W., HARRIS, J.R., MILNES, A.R. & VEEH, H.H. 1981: Bacterial origin of East Australian continental margin phosphorites. Nature 294, 442–444.

OFFICE CHERIFIEN DES PHOSPHATES, CASABLANCA, MOROCCO 1989: The phosphate basins of Morocco. In: Phosphate Deposits of the World. Vol. 2. Phosphate Rock Resources (Ed. by A.J.G. NOTHOLT, R.P. SHELDON & D.F. DAVIDSON). Cambridge Univ. Press, Cambridge, 301–311.

OPPENHEIMER, C.H. 1958: Evidence for fossil bacteria in phosphate rocks. Inst. Mar. Sci. Publ. 5, 157–159.

OUWEHAND, P.J. 1987: Die Garschella-Formation ("Helvetischer Gault", Aptian-Cenomanian) der Churfirsten-Alvier Region (Ostschweiz). Sedimentologie, Phosphoritgenese, Stratigraphie. Ph. D. Thesis. ETH Zürich Nr. 8409.

PICKERING, K.T. & STOW, D.A.V. 1986: Inorganic major, minor and trace element geochemistry an clay mineralogy from the Deep Sea Drilling Project Leg 96, Gulf of Mexico. Initial Reports DSDP 96, 733–746.

POUTANEN, E.-L. & MORRIS, R.J. 1983: The occurrence of high molecular weight humic compounds in the organic-rich sediments of the Peru continental shelf. Oceanol. Acta 6, 21–28.

POWELL, T.G., COOK, P.J. & McKIRDY, D.M. 1975: Organic geochemistry of phosphorites. Relevance to petroleum genesis. Amer. Assoc. Petroleum Geol. Bull 49, 618–663.

PRÉVÔT, L. & LUCAS, J. 1986: Microstructure of apatite-replacing carbonate in synthesized and natural samples. J. Sed. Petrol. 56, 153–159.

PRÉVÔT, L., EL FALEH, E.M. & LUCAS, J. 1989: Details on synthetic apatites formed through bacterial mediation: Mineralogy and chemistry of the products. In: Apatite and Phosphorites (Ed. by J. LUCAS, P.J. COOK & L. PRÉVÔT). Sci. Géol. Bull. Strasbourg 42, 237–254.

PRICE, N.B. & CALVERT, S.E. 1978: The geochemistry of phosphorites from the Namibian shelf. Chem. Geol. 23, 151–170.

RAO, V.P. & NAIR, R.R. 1988: Microbial origin of the phosphorites of the western continental shelf of India. Mar. Geol. 84, 105–110.

RASHID, M.A. 1985: Geochemistry of Marine Humic Compounds. Springer-Verlag, New York.

REDFIELD, A.C. 1958: The biological control of chemical factors in the environment. Amer. Scientist 46, 205–222.

REIMERS, C.E. & SUESS, E. 1983: Late Quaternary fluctuations in the cycling of organic matter off Central Peru: A proto-kerogen record. In: Coastal Upwelling: Its Sediment Record. Part A: Responses of the Sedimentary Regime to Present Coastal Upwelling (Ed. by E. SUESS & J. THIEDE). Plenum Press, New York, 497–525.

REIMERS, C.E., KASTNER, M. & GARRISON, R.E. 1990: The role of bacterial mats in phosphate mineralization with particular reference to the Monterey Formation. In: Phosphate Deposits of the World. Vol. 3. Neogene to Modern Phosphorites (Ed. by W.C. BURNETT & S.R. RIGGS). Cambridge Univ. Press, Cambridge, 300–311.

RIGGS, S.R. 1979: Petrology of the Tertiary phosphorite system of Florida. Econ. Geol. 74, 195–220.

ROBASZINSKY, F. 1989: The phosphatic chalk of the Mons Basin, Belgium. In: Phosphate Deposits of the World. Vol. 2. Phosphate Rock Resources (Ed. by A.J.G. NOTHOLT, R.P. SHELDON & D.F. DAVIDSON). Cambridge Univ. Press, Cambridge, 370–375.

ROMANKEVICH, E.A. 1984: Geochemistry of Organic Matter in the Ocean. Springer-Verlag, Berlin.

ROSENBERG, R., ARNTZ, W.E., DE FLORES, E.C., FLORES, L.A., CARBAJAL, G., FINGER, I. & TATAZONA, J. 1983: Benthos biomass and oxygen deficiency in the upwelling system off Peru. Jour. Mar. Res. 41, 263–279.

RUTTENBERG, K.C. 1990: Diagenesis and Burial of Phosphorus in Marine Sediments, Ph. D. Thesis. Yale University.

– 1992: Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnol. Oceanogr. 37, 1460–1482.

RUTTENBERG, K.C. & BERNER, R.A. 1993: Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. Geochim. Cosmochim. Acta 57, 991–1007.

SALOMON, D. 1989: Paleoecology and environmental analysis of the Lower Cretaceous shallow-marine Drusberg and Schrattenkalk facies of the Gottesacker area (Allgäu/Vorarlberg). In: Cretaceous of the Western Tethys (Ed. by J. WIEDMANN). Proc. 3rd Int. Cretaceous Symp., Tübingen 1987. Stuttgart, 353–375.

SAMB, M. 1983: Typologie et Caractérisation Physico-Chimique de Particules Phosphatées, Application à la Série Phosphatée Eocène de Casamance (Sénégal). Ph. D. Thesis. Université d'Orléans, Orléans.

SANDSTROM, M.W. 1980: Organic geochemistry of some Cambrian phosphorites. In: Advances in Organic Geochemistry 1979 (Ed. by A.G. DOUGLAS & J.R. MAXWELL). Pergamon Press, Oxford, 123–131.

– 1986: Proterozoic and Cambrian phosphorites – Specialist studies: Geochemistry and organic matter in Middle Cambrian phosphorites from the Georgina Basin, Northern Australia. In: Phosphate Deposits of the World. Vol. 1. Proterozoic and Cambrian Phosphorites. (Ed. by P.J. COOK & J.H. SHERGOLD). Cambridge Univ. Press, Cambridge, 268–279.

– 1990: Organic matter in Modern marine phosphatic sediments from the Peruvian continental margin. In: Phosphate Deposits of the World. Vol. 3. Neogene to Modern Phosphorites (Ed. by W.C. BURNETT & S.R. RIGGS). Cambridge Univ. Press, Cambridge, 33–45.

SARIG, S., KAHANA, F. & LESHEM, R. 1975: Selection of threshold agents for calcium sulfate scale control on the basis of chemical structure. Desalination 17, 215–229.

SCHMITT, M. & SOUTHGATE, P.N. 1982: A phosphatic stromatolite *(Ilicta* cf. *composita* Sidorov) from the Middle Cambrian, northern Australia. Archerigna 6, 175–183.

SCHOPF, J.W. & WALTER, M.R. 1982: Origin and early evolution of cyanobacteria. The geological evidence. In: The Biology of Cyanobacteria. Blackwell, London, 543–564.

SCHRADER, E.L., FURBISH, W.J. MATTEY, D. & MAY, J.A. 1980: Geochemistry and carbonate petrology of selected sediment samples from Deep Sea Drilling Project Leg 54, Eastern Pacific. Initial Reports DSDP 54, 319–328.

SCHUFFERT, J.D. 1988: Multi-layered authigenic apatite formation off southern Baja California (Abstr.). EOS 69, 1235.

SENKOVSKY, A.YU. 1982: An electron microscopic study of shelf phosphorites of the Volhyn-Podolian and Fore-Carpathian Cretaceous. Geol. Zh. 4, 127–131 (in Russian).

SHELDON, R.P. 1981: Ancient marine phosphorites. Ann. Rev. Earth Planet. Sci. 9, 251–284.

– 1989: Phosphorite deposits of the Phosphoria Formation of Western United States. In: Phosphate Deposits of the World. Vol. 2. Phosphate Rock Resources (Ed. by A.J.G. NOTHOLT, R.P. SHELDON & D.F. DAVIDSON). Cambridge Univ. Press, Cambridge, 53–61.

SHIMMIELD, G.B. & MOWBRAY, S.R. 1991: The inorganic geochemical record of the northwest Arabian Sea: A history of productivity variations over the last 400 k.y. from Sites 722 and 724. Proc. Ocean Dril. Project, Sci. Results 117, 409–430.

SHOLKOVITZ, E.R. 1973: Interstitial water chemistry of the Santa Barbara Basin sediments. Geochim. Cosmochim. Acta 37, 2043–2973.

SHUKLA, M., TEWARI, V.C. & YADOV, V.K. 1986: Late Precambrian microfossils from the Deaoban Limestone Formation, Lesser Himalaya, India. Palaeobotanist 35, 347–356.

SIMKISS, K. & WILBUR, K.M. 1989: Biomineralization: Cell Biology and Mineral Deposition. Academic Press, San Diego.

SLANSKY, M. 1986: Geology of Sedimentary Phosphates. Elsevier, New York.

SMITH, E.A.H., MAYFIELD, C.I. & WONG, P.T.S. 1977: Colonization and decomposition of fish bone material in natural and synthetic aqueous solutions. Fisheries Res. Board Canada J. 34, 2176–2184.

SOUDRY, D. 1979: Intervention de schizophytes dans la phosphomicritisation des débris osseux. C.R. Acad. Sc. Paris 288, Sér. D, 669–671.

– 1987: Ultra-fine structures and genesis of the Campanian Negev high-grade phosphorites (southern Israel). Sedimentology 34, 641–660.

– 1992: Primary bedded phosphorites in the Campanian Mishash Formation, Negev, southern Israel. Sediment. Geol. 80, 77–88.

SOUDRY D. & CHAMPETIER, Y. 1983: Microbial processes in the Negev phosphorites (southern Israel). Sedimentology 30, 411–423.

SOUDRY, D. & LEWY, Z. 1988: Microbially influenced formation of phosphate nodules and megafossil moulds (Negev, southern Israel). Palaeogeogr. Palaeoclimat. Palaeoecol. 64, 15–34.

– 1990: Omission-surface incipient phosphate crusts on early diagenetic calcareous concretions and their possible origin, Upper Campanian, southern Israel. Sediment. Geol. 66, 151–163.

SOUDRY, D. & NATHAN, Y. 1980: Phosphate peloids from the Negev phosphorites. J. geol. Soc. London 137, 749–755.

SOUTAR, A. & CRILL, P.A. 1977: Sedimentation and climatic patterns in the Santa Barbara Basin during the 19th and 20th century. Geol. Soc. Am. Bull. 88, 1161–1172.

SOUTHGATE, P.N. 1980: Cambrian stromatolitic phosphorites from the Georgina Basin. Nature 285, 395–397.

– 1986: Proterozoic to Cambrian phosphorites – specialist studies: Middle Cambrian phosphatic hardgrounds, phoscrete profiles and stromatolites and their implications for phosphogenesis. In: Phosphate Deposits of the World. Vol. 1. Proterozoic and Cambrian Phosphorites (Ed. by P.J. COOK & J.H. SHERGOLD). Cambridge Univ. Press, Cambridge, 327–351.

– 1988: A model for the development of phosphatic and calcareous lithofacies in the Middle Cambrian Thorntonia Limestone, northeastern Georgina Basin, Australia. Austral. J. Earth Sci. 35, 111–130.

STROHL, W.R. 1989: *Beggiatoaceae*. In: Bergey's Manual of Systematic Bacteriology (Ed. by M.P. BRYANT, N. PFENNING & J.G. HOLT). Williams & Wilkins, Baltimore, 2089–2106.

SUESS, E. 1981: Phosphate regeneration from sediments of the Peru continental margin by dissolution of fish debris. Geochim. Cosmochim, Acta 45, 577–588.

SUESS, E. & MÜLLER, P.J. 1980: Productivity, sedimentation rate and sedimentary organic matter in oceans. II. Elemental fractionation. Colloques Internationaux C.N.R.S. No. 293, 17–26.

TEWARI, V.C. 1981a: The systematic study of Precambrian stromatolites from Gangolihat Dolomites, Kumaon Himalaya. Himalayan Geol. 11, 119–146.

– 1981b: The carbon and oxygen isotope trend of the Deoban-Blaini-Krol-Tal microbial carbonates from the Lesser Himalaya, India. Geosci. J. 12, 13–16.

– 1984a: The allochemical constituents and environment of deposition of Gangolihat Dolomite, Kuthpuria China area, Almora district, U.P. Geosci. J. 10, 43–54.

– 1984b: First record of *Conophyton* Maslov from Mussoorie syncline and its significance on the age of the Krol Formation. In: Sedimentary Geology of the Himalaya (Ed. by R.A.K. SRIVASTAVA). Curr. Trends Geol. 5, 203–207.

– 1984c: Discovery of Lower Cambrian stromatolites from Mussoorie Tal Phosphorite, Inida. Curr. Sci. 53, 319–321.

– 1989: Upper Proterozoic – Lower Cambrian stromatolites and Indian stratigraphy. Himalayan Geol. 13, 143–180.

– 1991a: Paleomicrobiology, paleoenvironment and isotope geochemistry of the stromatolitic carbonate chert phosphate association from Lesser Himalaya, India. Nat. Sem. App. Geomicrobiol. India, 93–107.

– 1991b: Ediacaran metaphytes and metazoans from the Lower Krol Formation, Lesser Himalaya. Workshop on Ediacaran Fauna and Precambrian-Cambrian Boundary, Nainital, 1–10.

– 1993: Precambrian and Lower Cambrian stromatolites of the Lesser Himalaya. Geophytol. 23, 19–39.

TEWARI, V.C. & JOSHI, M. 1994: Stromatolite microstructures; A new tool for biostratigraphic correlation from Lesser Himalaya. Him. Geol. Jour. (in press).

TEWARI, V.C. & QURESHY, M.F. 1985: Algal structures from the Upper Krol – Lower Tal Formations of Garhwal and Mussoorie syncline and their palaeoenvironmental significance. Jour. Geol. Soc. India. 26, 111–117.

TOERIEN, D.F., GERBER, A., LÖTTER, H. & CLOETE, T.E. 1990: Enhanced biological phosphorus removal in activated sludge systems. In: Advances in Microbial Ecology (Ed. by K.C. MARSHALL), Vol. 11. Plenum Press, New York, 173–230.

TRICHET, J. & DÉFARGE, CH. 1994: Non-biologically supported organomineralization. Proc. 7th Int. Symp. Biomineralization. Bull. Inst. Oceanogr. Monaco (in press).

TRICHET, J., RACHIDI, M. & BELAYOUNI, H. 1990: Organic geochemistry of phosphorites: Relative behaviors of phosphorus and nitrogen during the formation of humic compounds in phosphate-bearing sequences. In: Phosphate Deposits of the World. Vol. 3. Neogene to Modern Phosphorites (Ed. by W.C. BURNETT & S.R. RIGGS). Cambridge Univ. Press, Cambridge, 87–96.

VAILLANT, B. 1987: Étude Experimentale du Role de Flores Bactériennes dans la Formation de l'Apatite. Ph. D. Thesis. Université de Nancy, Nancy.

VALDIYA, K.S. 1972: Origin of phosphorite of the late Precambrian Gangolihat Dolomite of Pithoragarh, Kumaun Himalaya, India. Sedimentology 9, 115–128.

VAN CAPPELLEN, P. 1991: The Formation of Marine Apatite: A Kinetic Study. Ph. D. Thesis. Yale University.

VAN CAPPELLEN, P. & BERNER, R.A. 1988: A mathematical model for the early diagenesis of phosphorus and fluorine in marine sediments: Apatite precipitation. Am. J. Sci. 288, 289–333.

– 1991: Fluorapatite crystal growth from modified seawater solutions. Geochim. Cosmochim. Acta 55, 1219–1234.

VAN CAPPELLEN, P., & INGALL, E.D. 1994: Benthic phosphorus regeneration, net primary production, and ocean anoxia: A model of the coupled marine biogeochemical cycles of carbon and phosphorus. Paleoceanography (in press).

VAN CAPPELLEN, P., GAILLARD, J.-F. & RABOUILLE, C. 1993: Biogeochemical transformations in sediments: Kinetic models of early diagenesis. In: Interactions of C, N, P and S Biogeochemical Cycles and Global Change (Ed. by R. WOLLAST, F.T. MACKENZIE & L. CHOU). Springer-Verlag, Berlin, 401–445.

VARENTSOV, I.M. 1981: Geochemical history of post-Jurassic sedimentation in the Central Northwestern Pacific, Southern Hess Rise, Deep Sea Drilling Project Site 466. Initial Reports DSDP 62, 833–845.

– 1983: Geochemical history of post-Middle Jurassic Atlantic, Deep Sea Drilling Project Leg 71, Ba, Sr and major components. Initial Reports DSDP 71, Part 1, 423–442.

VARENTSOV, I.M., SAKHAROV, B.A., RATEEV, M.A. & CHAPOROV, D.YU. 1981a: Geochemical history of post-Jurassic sedimentation in the Central Northwestern Pacific, Northern Hess Rise, Deep Sea Drilling Project Site 464. Initial Reports DSDP 62, 805–832.

VARENTSOV, I.M., TIMOVEEF, P.P. & RATEEV, M.A. 1981b: Geochemical history of post-Jurassic sedimentation in the Central Northwestern Pacific, Western Mid-Pacific Mountains, Deep Sea Drilling Project Site 463. Initial Reports DSDP 62, 785–804.

VEEH, H.H., CALVERT, S.E. & PRICE, N.B. 1974: Accumulation of uranium in sediments and phosphorites on the south west African shelf. Mar. Chem. 2, 189–202.

VEIS, A. & PERRY, A. 1967: The phosphoprotein of the dentin matrix. Biochemistry 6, 2409–2416.

VERA, J.A. & MARTIN-ALGARRA, A.: Mesozoic stratigraphic breaks and pelagic stromatolites in the Betic Cordillera, Southern Spain. In: Phanerozoic Stromatolites II (Ed. by C. MONTY & J. SERFATI). Kluwer Acad. Press. (in press).

YANSHIN, A.L. & ZHARKOV, M.A. 1986: Phosphorus and Potassium in Nature. Trudy Inst. Geol. & Geophys. Izd. Nauka, Moscow (in Russian).

ZANIN, YU.N., LETOV, S.V., KRASILNIKOVA, N.A. & MITROV, YU.V. 1985: Phosphatized bacteria from Cretaceous phosphorites of East-European Platform and Paleocene phosphorites from Morocco. Sci. Géol. Mém. 77, 79–81.

ZANIN, YU.N., GORLENKO, V.M., MITOV, YU.V., KRASILNIKOVA, N.A. & LETOV, S.V. 1987: Bacteriomorphous structures in nodular and granular phosphorites. Geology & Geophysics, Akad. Nauk SSSR 2, 43–49 (in Russian).

ZIMMERLE, W. 1982: Die Phosphorite des nordwestdeutschen Apt und Alb. Geol. Jb. A65, 159–244.

ZWOLSMAN, J.J.G., BERGER, G.W. & VAN ECK, G.T.M. 1993: Sediment accumulation rates, historical input, postdepositional mobility and retention of major elements and trace metals in salt marshes of the Scheldt Estuary, SW Netherlands. Mar. Chem. 44, 73–94.