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# Phosphorus and phosphorites: Sedimentology and environments of formation

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*Key words:* Phosphorite, phosphate, phosphorus, sedimentology, classification environment, paleoceanography, organic-rich sediments, glauconite, upwelling, petrology, geochemistry, isotopes

## ABSTRACT

Phosphatic sediments form not only beneath upwelling systems, but also on oceanic islands, atop seamounts, guyots and plateaus, and on some shelves, slopes and in epeiric environments that may not have experienced upwelling at all. We evaluate the formation of phosphorites and the sources of phosphorus in each of these settings. We define primary phosphogenesis, which produces primary phosphorite, as the process of carbonate fluorapatite precipitation within sediments, at the sediment/water interface and/or during diagenesis. Primary phosphogenesis is distinct from the hydraulic and biological reworking processes by which phosphatic grains are concentrated into granular phosphorite. Non-transported phosphorites may occur in any or all of the principal phosphorite settings. Granular phosphorites, which we believe are derived from primary phosphorites, are accumulations which developed on ancient shelves and in epeiric seas and appear to dominate phosphorite occurrences in the Phanerozoic record. These are variously cemented phosphorite siltstones, sandstones and conglomerates composed chiefly of phosphatic particles, many of which show some evidence of transport and deposition under the influence of bottom currents. Current activity plays an important role for many phosphorite deposits, not only for concentrating dispersed authigenic precipitates, but also for prolonging phosphate precipitation at critical shallow burial levels. In some cases, redeposition as phosphorite turbidites and tempestites has also been important. We summarize 13 important topics which require future research.

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## ZUSAMMENFASSUNG

Phosphatische Sedimente bilden sich nicht nur unterhalb von Zonen aufsteigender Tiefenwässer, sondern auch auf ozeanischen Inseln, auf Seamounts, Guyots und submarinen Tafelbergen, auf dem Schelf und an Abhängen sowie in flachen Epikontinentalseen, welche nie von aufsteigenden Tiefenwässern beeinflusst werden. Die Bildung der Phosphorite sowie die Phosphorquellen in jedem dieser Gebiete sollen hier diskutiert werden. Die Bildung der Phosphatgenese, welche den primären Phosphorit produziert, sei hier definiert als Prozess der Ausfällung von Karbonat-Fluorapatit innerhalb des Sediments, an der Sediment/Wasser-Grenze und/oder während der Diagenese. Primäre Phosphatgenese muss unterschieden werden von hydraulischen und biologischen Aufarbeitungsprozessen, bei welchen phosphatische Partikel zu granularem Phosphorit konzentriert werden. Nicht transportierte Phosphorite können in jedem der hauptsächlichlichen Phosphorit-Milieus auftreten. Granulare Phosphorite, von welchen wir annehmen, dass sie ursprünglich von primären Phosphoriten stammen, sind Anhäufungen, welche sich auf alten Schelfen und in flachen Epikontinentalseen bilden und welche die phanerozoischen Phosphoritvorkommen dominieren. Hier handelt es sich um unterschiedlich zementierte phosphoritische Siltsteine, Sandsteine und Konglomerate, welche hauptsächlich aus phosphatischen Partikeln bestehen. Einzelne zeigen Strukturen, welche auf Transport und Ablagerung unter dem Einfluss von Bodenströmungen hindeuten. Die Wirkung von Strömungen ist für viele Phosphoritablagerungen wichtig, nicht nur um verteilt auftretende authigene Körner zu konzentrieren, sondern auch um die Phosphatfällung innerhalb der kritischen Tiefe im Sediment zu verlängern. In bestimmten Fällen dominiert Umlagerung durch phosphoritische Turbidite. Zum Schluss werden 13 wichtige Themen zusammengefasst, die in Zukunft noch genauer erforscht werden sollen.

## Introduction

This paper presents results of a working group of IGCP project 325 members who met in Interlaken, Switzerland, in September 1993 to discuss modern concepts and controversies which surround the origin of marine phosphorites and their main component mineral, carbonate fluorapatite ( $\text{CFA} = \text{Ca}_{10-a-b-c}\text{Na}_a\text{Mg}_b(\text{PO}_4)_{6-x}(\text{CO}_3)_{x-y-z}(\text{CO}_3 \cdot \text{F})_y(\text{SO}_4)_z\text{F}_2$ , where  $x = y + a + 2c$ ;  $c$  is the number of Ca vacancies; Nathan 1984). Phosphorus is present in most rocks in minor amounts, but in phosphorites the amount of  $\text{P}_2\text{O}_5$  generally exceeds 18% and may, on occasion, reach upwards of 40%. This feature alone makes these rocks truly unusual, both for their scientific interest and economic value. Phosphorite rock is mined and exploited as the world's major supply of phosphorus, an essential ingredient in the manufacture of fertilizers and phosphate-based chemicals.

Our knowledge about phosphorites has increased tremendously over the past 15 years. This paper outlines the present state of both our understanding and lack of understanding about the modes of origin of marine phosphorites and phosphatic sediments, particularly with respect to the sources of phosphorus for these deposits, the interpretation of their often unique sedimentology, and their paleoceanographic (Fig. 1) and paleogeographic settings. Insights into phosphogenesis discussed in this paper derives from two distinct yet overlapping approaches: (1) marine-based studies of modern phosphogenic environments, including solid phase and pore water geochemistry and (2) land and core-based studies of ancient phosphatic sediments, which integrate aspects of stratigraphy, sedimentary processes, sedimentary petrology and solid-phase geochemistry. Below, we include in our discussions the present concepts and controversies which stem from the marine phosphorus cycle, the significance of upwelling, the sedimentology of phosphorites, primary versus granular phosphorites, principal environments of phosphorites and their deposits, relationships to variations in sea level and sequence condensation, and phosphorite giant occurrences and their episodicity through time. We conclude with a list of 13 subjects which stand out as requiring future refinement and research. Two compan-

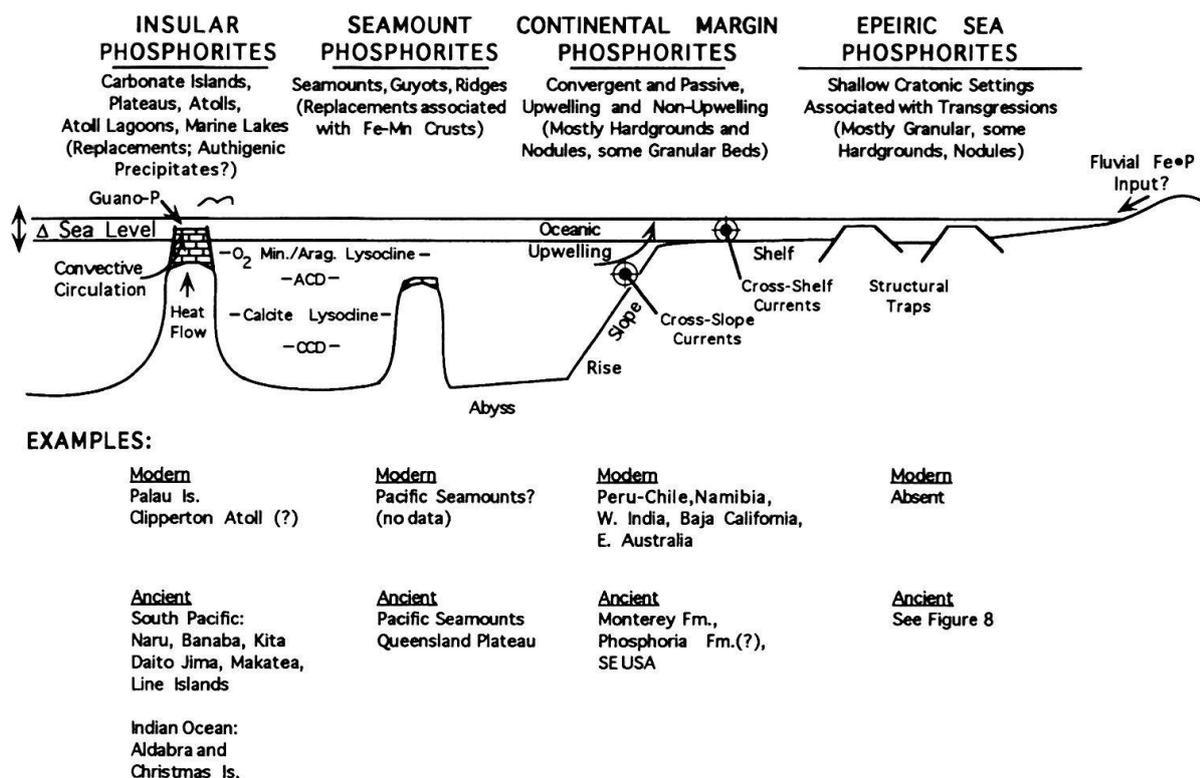


Fig. 1. Tectonic and oceanographic settings of marine phosphorites as derived from studies of the modern and ancient record.

ion papers in this issue discuss in detail phosphorite geochemistry (Jarvis et al. 1994) and the known and potential roles played by microbes during phosphogenesis (Krajewski et al. 1994).

### The marine phosphorus cycle

The geochemical cycle of phosphorus is complicated and remains rather poorly understood. Assuming a steady-state model for the modern, pre-industrial ocean, and assuming all major phosphorus input to the oceans from fluvial sources, Froelich et al. (1982) estimated the following proportionality between major marine outputs of reactive P to sedimentary reservoirs: (1) 40% as an output component associated with the burial of organic matter, (2) 40% removal of P as a component associated with CaCO<sub>3</sub> sedimentation (chiefly coccoliths and foraminifers), (3) about 11% removal in association with the sedimentation of metalliferous sediments around spreading ridges, (4) about 2% removal associated with the burial of fish debris (hydroxyapatite), and (5) perhaps ≤10% of the total oceanic P flux to sediments in association with the sedimentation and burial of phosphorites. Although dated (see Krajewski et al. 1994), the identification of the various sinks in this model remains instructive in that it serves to illustrate that an increase in efficiency of transfer of P into one sink may likely lead to a decrease in another. This

feature is important not only for viewing the long-term episodicity of phosphorite genesis (discussed below), but also because P is an important limiting nutrient intimately tied to the biochemical pathways of other elements and compounds, such as C, S, N, CO<sub>2</sub> and O<sub>2</sub> (e. g. see papers in Wollast et al. 1993). However, many of the exact flux rates and reservoir and residence times associated with this model remain poorly constrained, and the actual proportions between sinks now appear rather tenuous at best.

Mach et al. (1987) and Mackenzie et al. (1993) show significantly different estimates for the burial of organic P; furthermore, the modern abundance of phosphorite may actually be much greater than previously recognized (cf. Glenn et al. 1994, Filippelli & Delaney 1992, 1994a). Sherwood et al. (1987) showed that most of the P associated with foraminiferal tests in pelagic settings is actually that associated with iron oxides. In addition, although studies of phosphorites from both modern and ancient settings indicate active precipitation of carbonate fluorapatite within centimeters of the sediment-water interface, it should be borne in mind that precipitation of CFA and other forms of phosphorus adsorption may still occur deeper in the sediment column and in other environments that do not yield high concentrations of marine apatite, although perhaps not at high enough rates to prevent dilution by other components. Examples of such precipitation and burial include recent pore water and solid phase studies from open oceanic settings (e. g. Baturin 1988, Föllmi & von Breymann 1992, Filippelli & Delaney 1994b), and the recent recognition by Berner and colleagues (e. g. Berner 1990, Ruttenger 1992, Ruttenger & Berner 1993, Berner et al. 1993) that significant proportions of the global burial of phosphorus occurs as dispersed CFA precipitation and as iron-bound phosphate in large, high sedimentation-rate siliciclastic continental margin settings, such as deltas. Yanshin & Zharkov (1986) estimated that all Phanerozoic phosphorites contain about one million times less phosphorus ( $45 \times 10^9$  tones P<sub>2</sub>O<sub>5</sub>) as compared to its disseminated forms ( $85 \times 10^{15}$  tones P<sub>2</sub>O<sub>5</sub>). All these advancements are quickly changing the way we view the global inventory and cycling of phosphorus and its associated elements in the marine realm.

### **The upwelling model and other concepts**

The origins of phosphorites have been debated for well over one hundred years (see Gulbrandsen 1969, Bentor 1980, Sheldon 1981 and Cook et al. 1990, for historical reviews), and today the debates still continue. Every researcher studying phosphorites has been influenced in one way or another by the seminal works of Kazakov (1937, 1939), and subsequent workers, who proposed that these unusual sediments formed as a direct result of inorganic apatite precipitation from cold, ascending (upwelled) seawater. Kazakov suggested that during oceanic upwelling, a decrease in the partial pressure of CO<sub>2</sub>, and an accompanying increase in near-surface water's pH, resulted in a decrease in the solubility of these waters with respect to marine apatite (CFA). Thus, Kazakov concluded that phosphorites and their associated sediments (e. g. biosiliceous sediments and organic-rich shales) are intimately linked to upwelling and were thus formed in association with upwelling along continental margins (cf. Parrish & Curtis 1982, Parrish 1990).

Kazakov's "Upwelling Hypothesis" was later applied in a number of papers that sought to explain facies distributions and origin of phosphorites of the Permian-age Phosphoria Formation in western North America (e. g. McKelvey et al. 1953, McKelvey et al.

1959) and, subsequently, many other researchers compared still other phosphorite occurrences with those depicted in what eventually became known as the “Phosphoria Model” (Cook et al. 1990). Today, it is well known that many modern (Holocene age) phosphorites are indeed forming off coasts beneath upwelled waters, although for reasons different than earlier concluded by Kazakov. Many workers now believe that the key to the upwelling association in the modern setting, as well as the common association in the rock record between phosphorite, organic-rich shale and chert, is the transfer of phosphorus to sediments as a component of particulate marine sedimentary organic matter, the subsequent diagenetic degradation and release of dissolved inorganic phosphorus from these particles to sedimentary pore waters, and the eventual precipitation of CFA as an *in situ* diagenetic phase. Such precipitation may result in the formation of phosphorite hardgrounds, or as individual phosphate grains or concretions that may be concentrated by hydraulic processes to form granular phosphorite beds. Replacement of other phases, particularly carbonates, may also occur. Still, not all modern phosphorites appear to be forming beneath upwelling zones (Fig. 1), and the exact mechanism(s) by which phosphorus is supplied to pore waters or the sea floor, whether in upwelling zones or not, remains enigmatic. Other mechanisms for phosphate enrichment have been discussed, including microbial concentration, redox pumping of phosphorus via Fe-FeOOH redox pairs, fish bone dissolution, prolonged bathing of seamounts in oxygen-minimum zone waters, etc. These factors are not mutually-exclusive, and are discussed in the following sections. As we explore below, there actually appears to be a number of environments and pathways by which phosphorites and phosphatic sediments may form.

## **Sedimentology of phosphorites**

### *Primary phosphogenesis*

We define primary phosphogenesis in the marine environment as the process of apatite (usually CFA) precipitation within sediments, at the sediment/water interface and/or during diagenesis. Primary phosphogenesis – a biogeochemical process of precipitation influenced by such factors as bottom water and pore water redox potential and acidity, dissolved chemical species gradients and sedimentation rates – is distinct from the hydraulic and biological reworking/winnowing processes by which phosphatic clasts may be concentrated into granular phosphorite (discussed below).

Primary phosphorites are precipitates composed of CFA minerals formed physico-chemically or biochemically *in situ* in the marine environment and show little evidence for significant transportation. They may occur as primary phosphorite mud (“microphorite”, “phospholutite”), hardgrounds, concretions or nodules, microconcretions in muds (“pellets” in mudstones), and as lenses and layers in encasing sediments (e. g. Kennedy & Garrison 1975, Birch 1980, Manheim et al. 1980, Krajewski 1984, Von Rad & Rösch 1984, Cullen 1986, Glenn & Arthur 1988, 1990, Cook & O’Brien 1990, Garrison et al. 1990, Soudry 1992, Schuffert 1988, Föllmi et al. 1991, Föllmi & Garrison 1991, Glenn et al. 1994). In many cases, CFA appears to have precipitated directly from the dissolved phase, perhaps passing through an intermediate, non-crystalline precursor before reaching a more crystalline apatite (Baturin 1971, Gulbrandsen et al. 1984, Jahnke 1984, Lucas and Prévôt 1985, Froelich et al. 1988, Van Cappelen and Berner 1991, Krajewski et al.

1994). The occurrence of “mudstone phosphorites” in Vendian deposits of Mongolia (Ilyin & Ratnikova 1981), Middle Cambrian phosphorites of the Georgina Basin, Australia (Soudry & Southgate 1989), in the Miocene of Florida (Riggs 1979a, 1979b), and in the Neogene-Recent sediments of the southwest African and Peru continental margins (Baturin 1971, Glenn & Arthur 1988, Schuffert 1988, Glenn 1990b, Garrison & Kastner 1990, Glenn et al. 1994), suggests that one way phosphate commonly precipitates is as stratiform and/or concretionary association of microcrystallites. The common occurrence of phosphatic nodules and concretions of various size in mudrocks, which deform their surrounding laminations, also demonstrates their early diagenetic growth in soft sediment, prior to significant burial (e. g. Sheldon 1963, Heckel 1977, Struckmeyer 1982, Kidder 1985, Burnett et al. 1988, Garrison et al. 1990, Glenn & Arthur 1990).

Similar and overlapping with primary phosphorites are other phosphorites that occur as microbial CFA layers, coatings or crusts (e. g. Southgate 1986a, 1986b, Soudry & Champetier 1983, Lamboy 1990, Abed & Fakhouri 1990, Lewy 1990, Soudry & Lewy 1988), impregnations and replacements in lithified carbonates (e. g. Stumm & Leckie 1970, Kennedy & Garrison 1975, Jarvis 1980a,b, 1992, Glenn & Kronen 1993), phoscretes (Southgate, 1986a,b) and CFA precipitates within bioclasts (e.g. Lamboy 1987, Föllmi 1989). Non-transported (“pristine”) phosphorites may occur in any or all of the four principal phosphorite settings depicted in figure 1, although insular and seamount settings are usually dominated by them. Many are believed to be associated with stratigraphic condensation, depositional hiatuses and/or unconformities. Primary mudstone and stromatolitic phosphorites dominate Proterozoic phosphorite sequences (Trueman 1971; see papers in Cook & Shergold 1986a).

### *Granular phosphorites*

Granular phosphorites appear to dominate phosphorite occurrences in the Phanerozoic record and are often accumulations which developed on ancient shelves and in epeiric seas (Fig. 1). These are variously cemented phosphorite siltstones, sandstones and sometimes conglomerates, composed chiefly of phosphatic particles, many of which show some evidence of transport and deposition under the influence of bottom currents (see below). Cements are commonly carbonate, siliceous or phosphatic, and a clayey matrix is not uncommon.

The phosphatic grains (“allochems”) of granular phosphorites are usually dominated by what many workers refer to as “pellets” or peloids, which are spherical to subspherical silt- to pebble-sized grains consisting chiefly of carbonate fluorapatite, but often containing some admixtures of siliciclastic or carbonate debris. With some dissent, most researchers of our conference agreed that these grains are not of fecal origin (coprolites). This is suggested, for example, by the stable-isotopic analysis of individual “pellets” or bulk samples from both modern and ancient phosphorites which show them to be early diagenetic precipitates (e. g. Kolodny & Kaplan 1970, Al-Bassam 1980, McArthur et al. 1980, 1986, Benmore et al. 1983, Piper & Kolodny 1987, Glenn et al. 1988, Glenn & Arthur 1990, Morad & Al-Aasm 1994, see review in Jarvis et al. 1994). Structureless, concentrically coated (micro-banded), compound and intraclast grains are usually common, but primary phosphatic bioclasts such as inarticulate brachiopod fragments, vertebrate bones, teeth and fish scales also occur. Other phosphatic particles clearly have formed by

replacement of carbonate substrates, skeletal material or other allochems. Such grains are characterized by marginal or complete phosphate impregnation/replacement with various degrees of preservation of the primary structure (cf. Swett & Crowder 1982).

### *Phosphorite classification*

The wide range of very different particles and processes of formation complicates simple classification of phosphorites. Most attempts at classifying these rocks involves some modification of commonly used carbonate rock classification schemes. Riggs (1979a), for example, applied a modified Folk (1962) genetic carbonate classification to phosphorites, describing phosphorites by their orthochemical and allochemical constituents. Cook & Shergold (1986b) forwarded a scheme which is fundamentally based upon the Dunham (1962) textural carbonate classification (mudstone phosphorite, wackestone phosphorite, packstone phosphorite, grainstone phosphorite, boundstone phosphorite). As in carbonate petrology, where the Dunham scheme often has better applicability in the field and the Folk scheme advantages in optical microscopic work, both approaches will likely receive continued use in studies of phosphorites. Slansky (1986) suggested a scheme which combines elements borrowed from both Folk (1962) and Grabau (1904); he termed phosphorites 'phosphatites' and introduced terms such as biophosphalutite, intraphospharenite and oophospharudite. Broad, detailed treatments of the different kinds of phosphorites and their components can be found in synthesis treatises, such as Gimmel'farb et al. (1959), Mabie & Hess (1964), Trueman (1971), Cook (1976), Riggs (1979a), Baturin (1981), Slansky (1980, 1986) and Zanin (1987).

Garrison & Kastner (1990) recently created a broad descriptive system for the macroscopic description of Neogene-Recent Peru margin phosphates recovered from ODP cores (Fig. 2), which is also gaining useful applicability to land-based settings (e. g. Garrison 1992b):

1. ***F-phosphates***: small nodules, peloids or laminae of *friable*, light colored CFA. These were called colophon mudstones by Burnett et al. (1980). Consistency varies from very friable and unconsolidated to more compact, though even the latter can be scratched with a fingernail. Presumably, F-phosphates age or mature to eventually become D-phosphates.
2. ***D-phosphates***: well lithified, often dark and dense nodules, gravels and hardgrounds of CFA.
3. ***P-phosphates***: phosphoritic sands dominated by structureless and coated (microbanded) phosphatic grains, with some admixtures of fish bones and teeth.

Föllmi et al. (1991) defined three interpretative genetic classes into which many phosphate-bearing deposits may subsequently be placed (Fig. 3):

1. ***Pristine***: phosphates which lack any signs of reworking.
2. ***Condensed***: phosphatic laminae and particles which have concentrated by winnowing processes or bioturbation.
3. ***Allochthonous***: phosphatic particles that have been entrained by and redeposited from turbulent and/or gravity-driven flows.

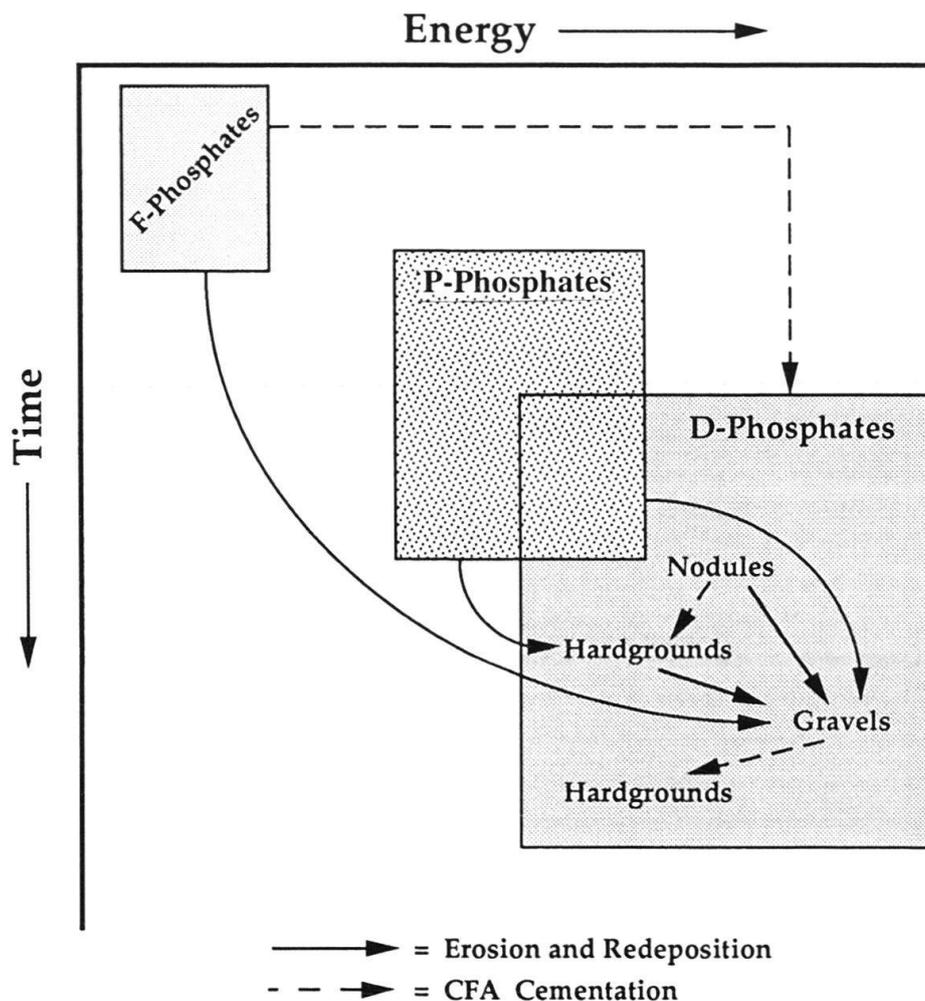


Fig. 2. Schematic portrayal of energy and time relationships for the formation and evolution of F-, P-, and D-phosphates. Shown also are the transitions among the three kinds of phosphorites that result from reworking and carbonate fluorapatite cementation on or near the sea floor. Modified from Garrison & Kastner 1990.

Hybrids of the Föllmi et al. three stratification types are common. For example, pristine phosphatic grains may experience redeposition, multiple episodes of burial, phosphatic cementation and subsequent erosional exhumation, to form a complex and laterally-variable phosphatic condensed bed.

#### *Phosphorites as a product of winnowing, reworking and grain transport*

Phosphorites often form stratified sediment bodies or unconformity-bound pavements as grain accumulates, pristine layers or concretions as well as multi-layered crusts or condensed beds. We believe that the geometry and internal structure of many phosphorite-bearing sediment bodies are an end product of syndepositional/early diagenetic precipitation of phosphatic minerals and subsequent syndepositional reworking processes.

The majority of economic phosphorites are granular deposits consisting of phosphatic pebbles or pelloidal sand-sized grains. Consequently, one critical problem in the sedimen-

Stratification in phosphatic sediments as a function of time and energy

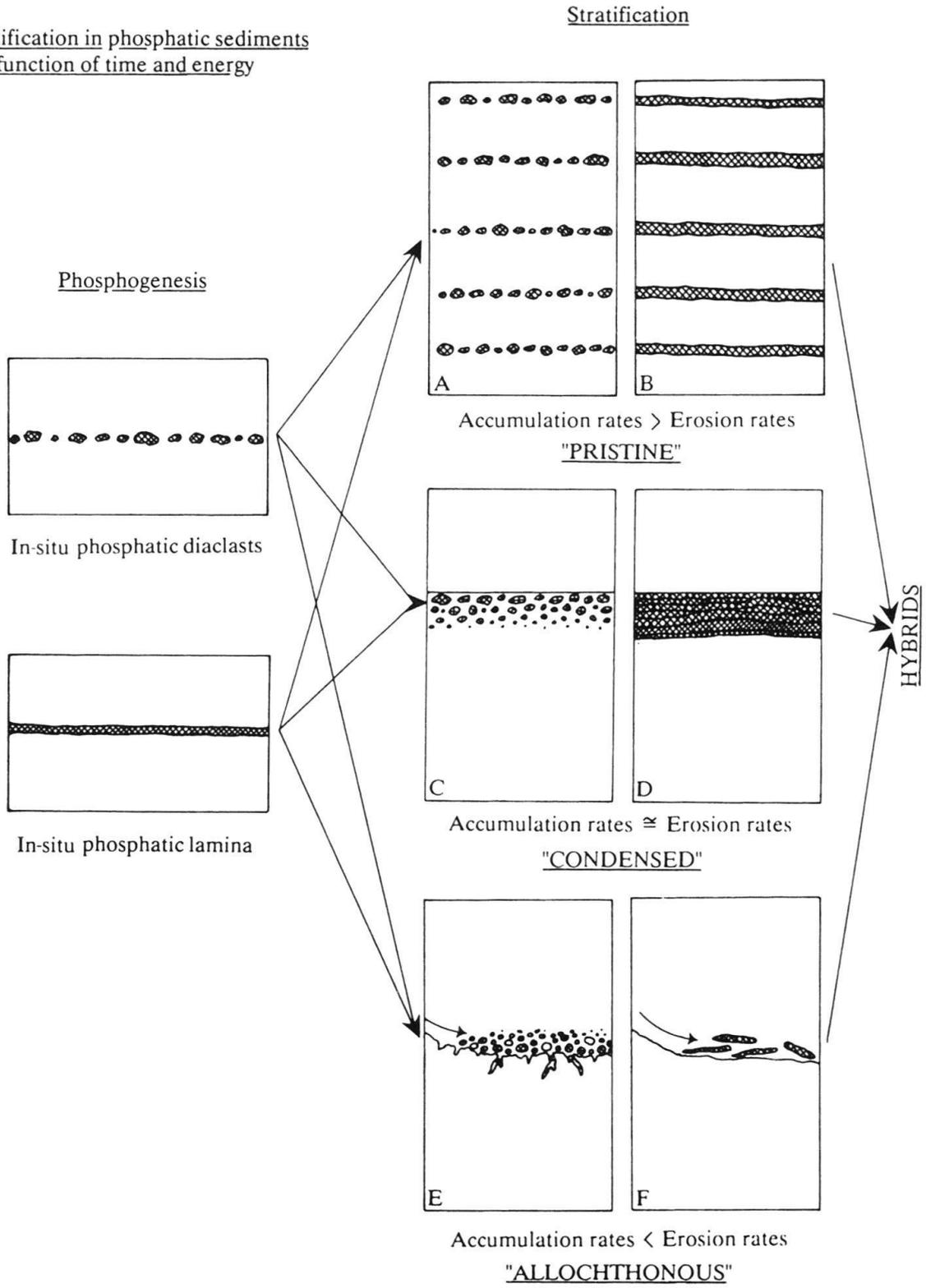


Fig. 3. Genetic classification of stratification types in phosphorites. From Föllmi et al. 1991, reprinted with permission of Springer-Verlag.

tology of phosphorites is determining if and how matrix-supported *in situ* phosphate grains or layers are concentrated into a grain-supported phosphorite. Penecontemporaneous post-depositional mechanisms which have been recognized include winnowing, reworking and redeposition.

Winnowing, which is the size selective sorting or removal of fines by aqueous processes, has been suggested to play an important role for many deposits (e. g. Sheldon 1957, Cook 1967, 1976, Riggs 1979a,b, Glenn & Arthur 1990, Glenn et al. 1994). The coupling of primary phosphogenesis followed by winnowing was initially expounded by Baturin (1971, 1981, Baturin & Bezrukov 1979), who defined a model of “highstand” phosphogenesis and “lowstand” reworking to account for Quaternary phosphorite encountered on the southwest Africa continental shelf. Yet, although such a two-step mechanism (primary phosphogenesis followed by reworking) for the accumulation of granular phosphorites in ancient rock suites is now largely accepted, only rarely has the primary phosphatic mud, the parental sediment for these redeposited phosphatic grains, been found in the accompanying stratigraphic record.

Föllmi (1989, 1990) credited winnowing by shelf-parallel currents to account for mid-Cretaceous phosphatic pebble beds in the Helvetic Shelf province of the northern Tethyan margin of western Austria. The presence of phosphatized ammonites from several different biostratigraphic zones within some of these condensed beds suggests that stratigraphic condensation (e. g. very low or negative sediment accumulation rate), accomplished by multiple episodes of primary phosphogenesis, shallow burial and hydraulic reworking, played a role in forming these stratigraphic markers (Föllmi 1989, 1990). In the Upper Cretaceous of Egypt, *in situ* pristine phosphate micro-concretions found in organic-rich shales and porcelanites appear to be the source rocks from which intimately associated granular phosphorites were derived through hydraulic winnowing and reworking (Glenn 1990a, Glenn & Arthur 1990). There, the ultimate end product of reworking is a variety of granular phosphorite beds, ranging from thin centimeter-thick lenticular phosphorite stringers in mud rocks and porcelanites, to large amalgamations forming fields of giant cross bedded phosphorite sand waves up to 10 m thick. In neighboring Israel, thin lenticular nonpelletal phosphorite beds occurring on structural highs also appear to have been a primary source for the penecontemporaneous granular deposits accumulating adjacent to them in structural lows (Soudry 1992). Similar margin to basin phosphate grain supply has also been envisioned for the Miocene deposits of Florida (Riggs 1979a, 1979b) and California (e. g. Garrison et al. 1987, Garrison 1992a, 1992b). The Meade Peak and Retort members of the Permian Phosphoria Formation are dominated by mudstones, phosphatic mudstones, argillaceous phosphorites and granular phosphorites (McKelvey et al. 1959). The Meade Peak member grades from non-carbonaceous crossbedded and well sorted phosphorites with abraded grains in nearshore regions to carbonaceous, pyritic phosphatic mudstones in offshore areas and the unit reaches a maximum thickness along the hinge-line separating the nearshore and offshore facies. The common interbedding of phosphatic mudstone and phosphorite, the vertical gradation of phosphorite into phosphatic mudstone, the presence of silt and clay inclusions in apatite pellets of phosphorites that contain little or no detritus in their matrix, as well as the abraded character of the fossils within the phosphorites compared with that of the mudstones suggests that the Meade Peak phosphorites were derived from winnowing and reworking the phosphatic mudstones (Sheldon 1957, reiterated in McKelvey 1959). “Bone beds”, containing

high concentrations of vertebrate skeletal fragments and fish teeth, interpreted by some as representing mass-mortality events, may also occur as a product of hydrodynamic sediment sorting.

Allochthonous phosphorite turbidites have been described, including the upper Cretaceous of Colombia (Föllmi et al. 1992), Oligo-Miocene strata of Baja California Sur, Mexico (Galli-Oliver et al. 1990) and the Cretaceous of Israel, Egypt and Jordan (see Kolodny & Garrison 1994, Glenn et al. 1994 and Abed 1994, respectively). Allochthonous phosphorite tempestites have been interpreted from the Eocene of Morocco (Trappe 1991, 1992). As we noted above, granular phosphorites in many settings appear to have accumulated within structural lows or "traps" (Fig. 1). "Classic" examples include Coniacian deposits in Gabon (Slansky 1986), Eocene deposits of Senegal, Nigeria and Morocco (Slansky 1986; see however, Herbig & Trappe, in press, for an alternate interpretation), and Neogene continental borderlands of California and the Late Cretaceous Mishash Formation of Israel (see Kolodny & Garrison 1994, for review). In some cases, sediment gravity flows ("phosphatic turbidites") apparently entrained live adult callianassid tracemakers, which created distinctive burrows when they were redeposited with the event beds (Föllmi & Grimm 1990, Grimm & Föllmi 1994). Thus, depositional and biological amalgamation of tractional event deposits (cf. Dott & Bourgeois 1982) have played an important role in the accumulation of some thick peloidal phosphorite beds (Grimm 1992); such processes need further assessment in other settings.

#### *Phosphorus and Microbes in Sediments*

The primary genesis of at least some phosphorites is linked to the microbial decomposition of organic matter within sediments. This takes place as microbes decompose organic matter to release phosphorus to pore waters, or as a byproduct of such reactions wherein adsorbed phosphate is released from hydrous ferri-oxide minerals upon oxidative reduction. However, syndepositional concentration of phosphorus may also be accomplished through microbial and/or microbial-influenced biogeochemical pathways. Reimers et al. (1990) illustrated how modern sulfur-oxidizing bacteria of the genus *Beggiatoa* concentrate P within their tissues at 3 to 6 times above the level found in planktonic marine organic matter. The interpretation of "microbial structures" of different types in phosphorites is widespread (Soudry 1987, Soudry & Champetier 1983, Lamboy 1990, Abed & Fakhouri 1990), but the role which microbes play is problematic to assess, since there are many different types and functions and, taken together, they may lie somewhere along a continuum ranging between passive associates to the process of phosphogenesis and active apatite biomineralization. In fact, the role of microbial communities may vary dramatically in differing temporal and/or depositional settings; for example, the in-vivo release of phosphate through certain microbial groups upon transfer into anoxic environments (Gächter et al. 1988, Gächter & Meyer 1993). Microbial structures are evident in pristine phosphatic nodules and stringers within phosphatic marlstones of the Miocene Monterey Formation of California, yet their significance requires further exploration (Williams & Reimers 1983, Reimers et al. 1990, cf. Grant 1991). Krajewski et al. (1994) explore the relationships between microbes and phosphogenesis more fully in their companion paper to this. There, they conclude that microbial communities help control the rates and mechanisms by which phosphorus concentrations are elevated in pore waters,

but that there is no convincing evidence of other important microbial effects being directly involved in the formation of CFA in marine sediments, for instance intra-cellular precipitation of calcium phosphate.

### **Principal environments of phosphogenesis and their deposits**

#### *Insular phosphorites*

Most insular phosphorites are believed to be those formed as a result of the alteration of phosphatic and nitrogenous bird droppings to apatite (usually CFA with various substitutions) on oceanic islands and atolls. Hutchinson (1950) described two types: thin, young (3–5 Ka, Veeh 1979) accumulations on atolls or low-lying islands and thicker, older (>800 Ka, the limit of dating technique; Veeh 1979) deposits lying on higher islands with more than 50 m of relief. The disparity in the age of these two types of deposits remains unresolved. Through leaching by meteoric water, these deposits can form thin to thick cemented phosphatic crusts and, in some cases, the leached solutions result in phosphatization of underlying limestones. Small, isolated cave deposits that result from bat droppings also occur (see Hutchinson 1950). Discussions of the relationships between weathering and the alteration and production of phosphate minerals are given in Altschuler (1973) and Flicoteaux & Lucas (1984).

Large insular deposits attributed to bird guano occur in Curacao, Dutch Antilles; Christmas Island, Indian Ocean; Makaeta, French Polynesia; Kita Daito Jima and Okino Daito Jima, NW Pacific; Anguar, SW Pacific and on Ocean Island and Nauru, Central Pacific (Cook 1984). The deposits of Nauru are (were) of the largest insular occurrences known; the original reserves were estimated at 90 million tons (Hutchinson 1950), of which now perhaps 10% remains after mining. The deposits of Nauru consist of layers of pelletal and pelleted conglomeratic phosphorite draped over a dolomite karrenfeld. The petrography and mineralogy of these deposits and many other insular occurrences is remarkably similar to that of many ancient and modern continental margin and epeiric sea phosphorites (finely laminated phosphorite and structureless, nucleated and concentrically-banded carbonate fluorapatite pellets; McClellan & Lehr 1969, Aharon & Veeh 1984, Piper et al. 1990, Rossfelder 1990), yet their minor element and stable isotope geochemistry indicate that guano reacted with rainwater to produce a phosphate-charged solution that precipitated apatite within the zone of fresh ground waters (Piper et al. 1990). Deposits on other islands include iron and aluminium phosphates when the underlying substrate is rich in aluminosilicates (Burnett 1980, Piper et al. 1990).

Hutchinson (1950) hypothesized that insular deposits occur only where large birds feed over wide trophic fields and return to an isolated locale for rest and reproduction. Presumably exemplary deposits are the coastal islands of Peru and Chile for which Hutchinson (1950) calculated guano accumulation at rates of several meters per 100 years. Hutchinson (1950) also believed that certain geologic criteria must also be met for insular phosphorite accumulations, such as a suitable substrate and a semi-arid climate which meets the requirement for leaching but with rainfalls low enough as to prevent entirely washing the deposits away. The primary prerequisites for the formation of insular guano phosphorites, therefore, appear to be the presence of isolated islands with relatively dry climates and within close proximity to upwelling centers. However, the large island phosphorite deposits

on Nauru, Ocean, Makatea and Christmas Islands are located in areas that at present do not meet these conditions and thus may represent fossil deposits that formed when climate conditions were more favorable than today (Burnett 1980; also see discussions of phosphorites on wet islands in Stoddart & Scoffin 1983). On the basis of isotope studies, Aharon & Veeh (1984) proposed that drier climatic conditions existed in the tropics during Quaternary ice ages associated with the extension of equatorial upwelling in the Pacific.

#### *Alternate models and remaining questions about insular phosphorites*

Burnett & Lee (1980) pointed out some of the unanswered intriguing questions about insular phosphorites include the origin of the karrenfeld commonly found on limestone islands, the lack of bird fossils within any of the deposits, the origin of the phosphate materials, a means of introducing elements such as uranium and fluorine into the phosphate minerals, and the broad climatic and temporal zonations associated with them. Not all workers agree that the accumulation of bird guano is the primary prerequisite for the origin of insular phosphorites, and this debate dates back over 50 years (e. g. Ellis 1936). Bourrouilh-Le Jan (1980), for example, questioned the guano hypothesis for the "classic" deposits on Nauru, and others have pointed out that some insular phosphorite deposits do not occur amidst eutrophic upwelling settings, but rather in oligotrophic "oceanic deserts". In marked contrast to the guano model, Rougerie & Wauthy (1989) suggested that the formation of phosphorites atop atolls is a consequence of what they term endo-upwelling (a. k. a. Kohout flow), which involves geothermally driven, upward transport of nutrient-rich intermediate waters through the structure of atolls and up to their enclosed lagoons. Some support for this model (Rougerie & Wauthy 1989) stems from the trace element composition (Zn, Ni, La; Bourrouilh-Le Jan 1980) of phosphorites from Clipperton atoll that appear to be derived from the atoll's volcanic pedestal. Interestingly, however, the lagoon waters on Clipperton atoll are meromictic (periodically anoxic; Bourrouilh-Le Jan et al. 1985), suggesting elevated primary production and stratification, and Piper et al. (1990) used this aspect of the Clipperton atoll as an element in their model of the evolution of the Nauru sequence. In further contrast, phosphorite appears to be forming today within sediments of a tropical anoxic marine lake on Palau in the southwest Pacific (Burnett et al. 1989), where elevated primary productivity is maintained by phosphorus input from surrounding jungles (Hamner et al. 1982; W.C. Burnett, per. comm.). Differentiation between the timing and modes of formation of insular deposits and their relation to climatic variability remains an important problem in phosphorite research.

#### *Seamount and Guyot phosphorites and Fe/Mn crusts*

Phosphorites and phosphatized limestones are also common features of seamounts, ridges and other elevated portions of the sea floor throughout the world's oceans, and many of these are associated with iron-manganese encrustations. Some of these deposits are buried (e. g. Glenn & Kronen 1993, Haggerty et al. 1993), but others occur directly on the elevated portions of the sea floor and may have done so for substantial portions of the Cenozoic (Burnett et al. 1987). Most are believed to be submarine in origin, they may be linked to the oxygen minimum zone (e. g. Halbach et al. 1982), and are typically characterized by very low sedimentation rates (e. g. De Carlo & Fraley 1992). Some workers at-

tribute their origin to submarine volcanic sources (e. g. Zelenov 1972, Safonov 1982). The mineralogy and major element chemistry of these deposits (Burnett et al. 1987) is similar to that of the phosphorites of continental margins, but, unlike the continental margin occurrences, are characterized by their association with manganese, low concentrations of organic carbon and uranium, an absence of pyrite and a relative enrichment of the rare earth elements (REE) in the heavy lanthanoids (Baturin 1981); seamount phosphorites display REE patterns like that of seawater (Kolodny 1981, Burnett et al. 1983), whereas continental margin phosphorites show typical "shale-like" REE patterns (McArthur & Walsh 1985; Piper et al. 1988). Based on the known distribution and geologic setting of seamount and other "open-ocean phosphorites", Burnett et al. (1987) reached the following conclusions:

- (1) Phosphorites and phosphatic rocks are common on many seamounts.
- (2) Most of these deposits are marine in origin, although some of these are clearly derived by submergence of insular phosphorites.
- (3) The present distribution of these deposits suggests that they may form preferentially at low latitudes, perhaps in response to equatorial upwelling and associated phenomena (high biological productivity and consequent development and maintenance of an oxygen minimum zone, etc.)
- (4) The association of phosphorite with iron-manganese crusts on seamounts in the Central Pacific Ocean is probably related to the enhanced concentrations of phosphate and metals within the zone of minimum dissolved oxygen which bathes the summits of many seamounts.

Cullen & Burnett (1986) observed environmental differences between the occurrence of phosphorites on isolated, peaked seamounts and somewhat shallower, flat-topped guyots that have experienced subaerial exposure and later subsidence. In particular, they suggested that in guyot settings, dolomite is a common co-occurrence, and that the apatite crystallites are small. The implication is that at least some of the guyot occurrences are submerged insular deposits formerly derived from bird guano and that the dolomite of these occurrences is related to shallow water dolomitization processes (cf. Morse & Mackenzie 1990).

Glenn & Kronen (1993) argued that ferroan dolomite and associated hardground Fe-phosphorite crusts of the Queensland Plateau of Australia were the result of submarine diagenesis within the oxygen-minimum zone in the Late Pliocene. They showed that these crusts were never shallower than upper bathyal depths and developed during a non-depositional period that correlated with global oceanic current activity and intensification of intermediate water mass flow strengths during the late Pliocene ice age transition. They also found evidence for aragonite dissolution and the precipitation of open marine sparry calcites in these crusts, which they attributed to a concomitant rise of the lysocline at this time (Farrell & Prell 1991). In this regard, it is noteworthy that Cullen & Burnett (1986) and Rao et al. (1992) also found anhedral to subhedral calcite crystals in the pores of seamount and guyot phosphorites.

Hein et al. (1993) examined phosphorites of Cretaceous seamounts in the Pacific and, on the basis of inferred strontium isotope ages of their CFA, suggested that most of these replaced carbonates during two periods, first in the Late Eocene/Early Oligocene and lat-

er in the Late Oligocene/Early Miocene. These workers also suggested that the development of this phosphorite occurred at times of climatic transition and increased oceanic circulation and that through fluctuations in the CCD and lysocline, intermediate waters became increasingly corrosive, thereby favoring the replacement process. These workers are thus largely consistent with the interpretations of Glenn & Kronen (1993).

McMurtry et al. (1994), however, suggest that strontium isotopes ages of seamount phosphorites may be in error (including their own) and by using microfossil dating constraints, found that tectonically back-tracking seamounts to their time of phosphogenesis placed them within 10°N of the equator, consistent with a mechanism of upwelling-enhanced productivity and reduced oxygen associated with equatorial divergence.

#### *Modern continental margin phosphogenic environments*

The known distribution of modern (presently-forming) continental margin phosphorites is shown in figure 4. Most of these occur as phosphate nodules and crusts, and occasionally as phosphorite sands, that are found on slopes and shelves beneath upwelled waters along the west coasts of South America (Peru-Chile), southwest Africa, Baja California and India. Pleistocene-Recent deposits also occur along the eastern margin of Australia (New South Wales), but these apparently differ in that they occur beneath waters that do not sustain high levels of primary productivity. Because most recent research on modern/subrecent deposits has centered on the eastern boundary current upwelling site off Peru-Chile and the non-upwelling western boundary current site off the east coast of Australia, we contrast these instructive occurrences below.

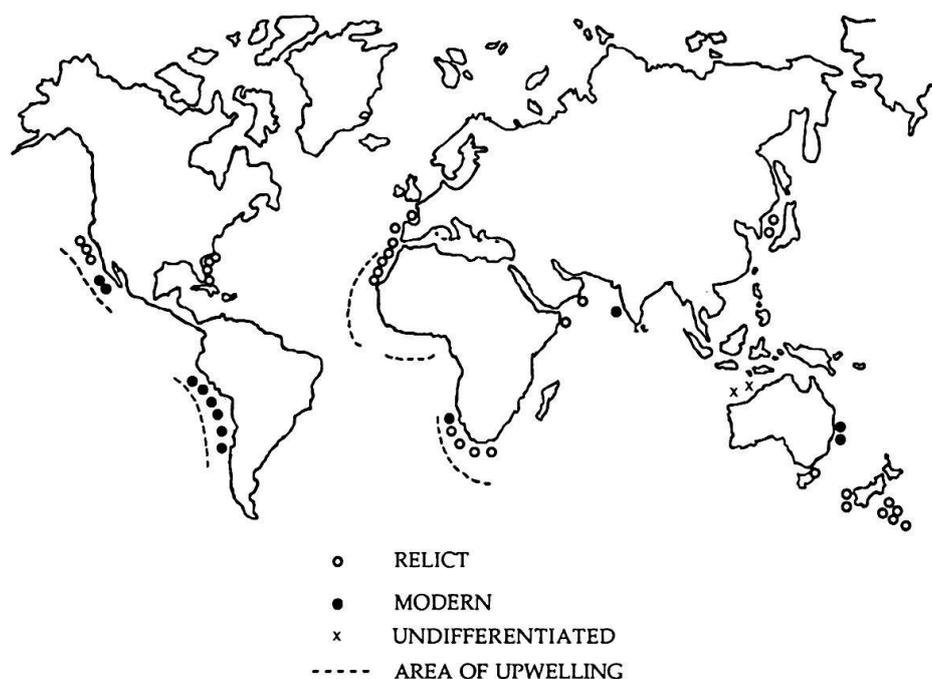


Fig. 4. Location of modern and relict continental margin phosphorite deposits on today's sea floor. Continental margin upwelling centers are indicated.

## Peru-Chile shelf and slope

The Peru margin has to date received closest study of all modern phosphorite occurrences and is a commonly-cited analog for ancient deposits. Phosphatic facies of the Peru continental margin (see papers in Burnett & Froelich 1988, Garrison & Kastner 1990, Glenn et al. 1994) chiefly reside on the upper slope-outer shelf within biosiliceous and organic-carbon-rich muds that result from low continental fluvial discharge, sustained nutrient upwelling and high biological productivity (Rosato 1974, Kriisek & Scheidegger 1983, Reimers & Suess 1983). The sediments are laminated to burrow-mottled (Garrison & Kastner 1990, Schrader & Sorknes 1991) and numerous erosional unconformities in the sediments suggest intermittent slope failure and scouring by bottom currents over periods of thousands of years (Devries & Percy 1982, Reimers & Suess 1983). Such variations between sedimentation and sediment reworking/winning have likely played a major role in concentrating pristine phosphate into reworked deposits, as well as serving as a mechanism for maintaining phosphatic phases at the very shallow burial levels apparently optimum for continued phosphate precipitation from pore waters (Froelich et al. 1988, Glenn & Arthur 1988, Glenn et al. 1988).

Phosphorite nodules, crusts and pelletal sand beds have been recovered from many locations along the Peru-Chile shelf and slope (see papers in Burnett & Froelich 1988, Garrison & Kastner 1990). Recent submersible studies (Arthur et al. 1993, Glenn et al. 1994) demonstrate that the shelf and slope off Peru is largely divided into cross-shelf/slope tracts of surface sediments dominated by organic-carbon-rich muds covered with benthic sulfide-oxidizing bacterial mats (*Thioploca* sp.) at shallower depths, extensive tracts of relatively mud-free zones of phosphatic crusts within the heart of the oxygen-minimum zone along the outer shelf and upper slope, and glauconite sands that occur along the base of the oxygen-minimum zone (Fig. 5). The sea floor along the upper slope is almost entirely covered with gravely phosphorites, phosphatic hardgrounds or pelletal sands; highest bottom water velocities were found to occur in association with the phosphorite and glauconite facies (Fig. 5). Lowest velocities typify the tracks of phosphorite-poor, organic-carbon-rich mud facies along the middle to outer shelf.

Burnett & Veeh (1977) and Burnett (1977) published seminal papers about the Peruvian occurrences that have strongly influenced our thoughts about phosphorites. They proposed an early diagenetic origin for the Peru Margin phosphorites, both on the sea floor, where the sea floor is impinged by the oxygen-minimum zone, and in oxygen-depleted pore-waters centimeters below the sediment/water interface. It was suggested from these earlier studies that at least 4 characteristics of anoxic (to sub-oxic) pore waters from the Peru-Chile shelf favored inorganic precipitation of carbonate fluorapatite: (1) high flux of dissolved inorganic phosphate in pore waters, (2)  $Mg^{2+}$  depletion during diagenesis to reduce its inhibition effect on apatite solubility (cf. Martens & Harris 1970, Savenko 1978, Van Cappellen & Berner 1991) (3) high pH and (4) suitable nucleation sites.

Since pore water composition reflects diagenetic reactions that transfer reactants and products between solid and dissolved phases, pore water studies provide insight into active phosphogenic processes. Peru Margin investigations associate phosphogenesis with high organic carbon burial rates and suboxic diagenesis. In suboxic sediment settings, microbially mediated respiration of organic matter drives elevation of dissolved phosphate

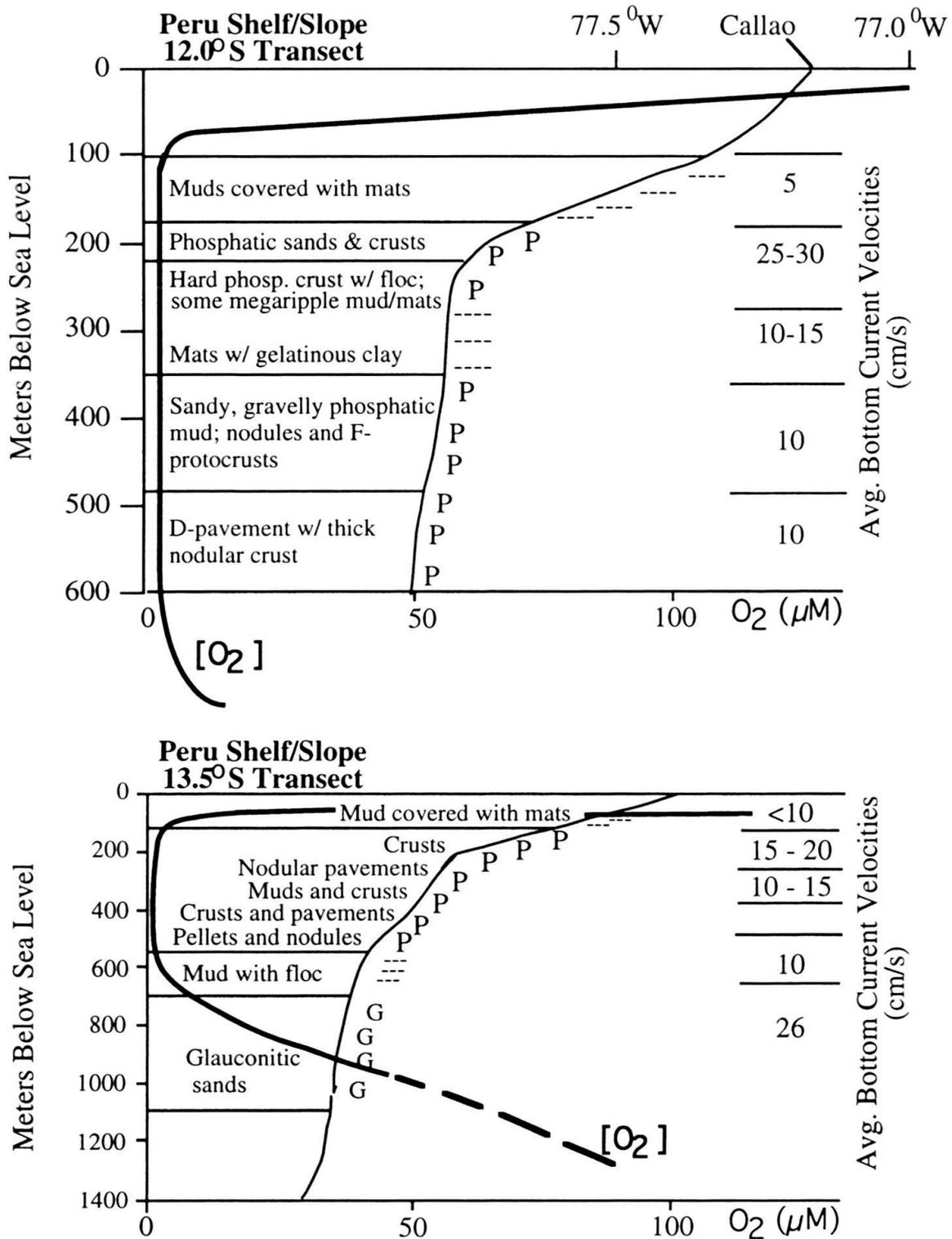


Fig. 5. Sediment and phosphorite distribution together with measured bottom current velocities (cm/s) and dissolved oxygen concentrations ( $\mu\text{M}$ ) on the outer Peru shelf and upper slope at 12°S (top) and 13.5°S (bottom) (results from R/V *Seward Johnson*, 1992 cruise; unpublished). "P" represents distribution of phosphorite. Nodular hardground pavements and phosphatic sands occur in association with highest current velocities. Friable (F-phosphate) CFA-protocrusts occur between about 350 and 500 m. Glaucinitic sands occur along the base of the oxygen minimum zone between 700 m and 1100 m at 13.5°S. Bacterial mats are sulfide-oxidizing *Thioploca* sp. After Glenn et al. 1994.

( $\text{PO}_4^{3-}$ ) in pore waters towards supersaturation with respect to apatite. Froelich et al. (1983, 1988) measured steep increases in dissolved phosphate in the upper few tens of centimeters of organic-rich sediments in the oxygen minimum zone off Peru and noted that pore water phosphate increased downcore to a maximum, below which  $\text{F}^-$  decreased in concert with declining dissolved phosphate concentrations. These authors suggested that the pore water distributions were reflecting the precipitation of CFA and considered that sea water-derived  $\text{F}^-$  in pore waters limited phosphogenesis to a zone of very shallow burial depth.

Glenn & Arthur (1988) and Glenn et al. (1988) demonstrated by solid phase and pore water geochemistry, isotopic studies and determination of textural parameters that carbonate fluorapatite (CFA) is precipitated within centimeters below the sediment-water interface, in minimally compacted gelatinous muds with high organic-carbon content and high porosity. In measuring the isotopic composition of deeper and older phosphorites recovered in Ocean Drilling Program cores, Leather & Kastner (1994) showed that these phases also represent very early diagenetic precipitates (although at deeper depths they may undergo diagenetic exchange). Froelich et al. (1988) stressed that phosphogenesis is limited by diffusive-access to the sediment-water interface and Glenn et al. (1988) also suggested that carbonate fluorapatite precipitation may be halted at greater depths in the sediment by lattice poisoning by excess dissolved  $\text{CO}_3^{2-}$ . On the basis of petrological and solid phase geochemical studies, Glenn & Arthur (1988) and Glenn et al. (1988) found a time-depth paragenetic sequence for modern primary Peru margin phosphorites and other authigenic phases. Glauconites were found to be precipitated relatively early following the partial reduction of ferric iron and, following this, phosphate, pyrite, and then dolomite precipitation take place at progressively deeper levels in the sediment column; glauconite and phosphate precipitation are more closely tied with suboxic diagenesis, pyrite with sulfate reduction, and dolomite with sulfate reduction and methanogenesis.

The above studies provide clear evidence that CFA precipitation occurs early in Peru muds. In both modern muds of Baja California (Jahnke et al. 1983, Schuffert 1988) and Peru (Froelich et al. 1988) it was also discovered that the earliest precipitation of CFA appeared to be associated with an interfacial spike of anomalously high dissolved phosphate at the sediment-water interface. The origin of this "P-spike" is still under investigation; it may be related to suboxic bacterial degradation, the dissolution of fish debris (Suess 1981, Van Cappellen & Berner 1988), "iron-pumping" (Fig. 6) which releases phosphate from iron oxides once they are reduced in pore waters (see below), the metabolic activity of sulfide-oxidizing or other bacteria, P release to solution by bacteria in response to redox changes (e. g. Gächter et al. 1988, Gächter & Meyer 1993, Ingall et al. 1993), or some other mechanism (also see Krajewski et al. 1994). In addition, Burnett et al. (1988) demonstrated that some pellets in the Peru margin muds grow very quickly – probably in less than 10 years – and can form highly concentrated sediment layers, perhaps in the absence of significant reworking (cf. Baker & Burnett 1988). These rapid rates appear to confirm other experimental and field-based evidence that magnesium inhibition of carbonate fluorapatite precipitation (Martens & Harris 1970, Atlas and Pykowitz 1977, Savenko 1978) may be overcome within a number of years (Gulbrandsen et al. 1984, Van Cappellen & Berner 1991).

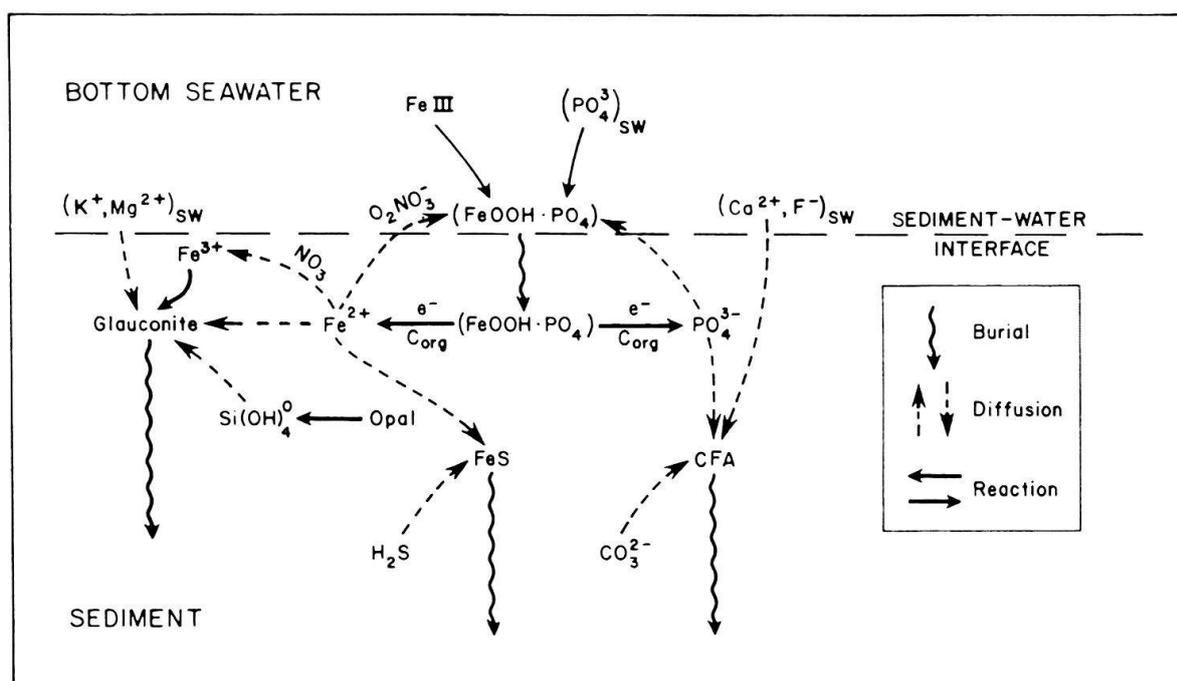


Fig. 6. Schematic diagram of iron redox-P cycle as postulated for Peru Margin sediments by Froelich et al. (1988). Iron hydroxyoxides sorb phosphate from bottom water and from upward diffusing pore water phosphate. Once reduced below the sediment-water interface these compounds release the sorbed phosphate to pore waters which is then precipitated. The reduced iron ( $\text{Fe}^{2+}$ ) fluxes back to the more oxidizing environment of the bottom waters, where it may again sorb phosphate, or is precipitated in the sediments as a component of pyrite or glauconite. A somewhat similar mechanism has also been proposed for the modern sediments of the east Australian margin (see text). Reprinted with permission of Elsevier Science.

### Modern non-upwelling continental margin environment: East Australia

Pleistocene-Recent phosphorite nodules from the eastern shelf of Australia are unique for their occurrence along a margin which lacks prominent coastal upwelling, high primary productivity, suboxic intermediate water masses and high organic carbon fluxes (O'Brien & Veeh 1980, 1983, Cook & O'Brien 1990). Upwelling in this setting is weak and sporadic to absent and organic carbon fluxes to the sediments are relatively low; the organic carbon content of the sediments associated with the Recent nodules is <0.5%, which contrasts markedly with that of the Peru margin where organic carbon contents vary between about 1–20%. Thus, the origin of the East Australian occurrences has posed an interesting challenge to the textbook concept that the formation of modern phosphorites takes place beneath upwelling zones and is fueled by high rates of phosphorus release to pore waters as a consequence of the microbial degradation of organic matter.

As encountered off Peru, different types of phosphorite nodules occur in this setting (O'Brien & Veeh 1980, O'Brien et al. 1990). Older nodules (> 60 Ka; "Type II") occur on the outer shelf and are iron-rich, highly indurated, and have a glazed appearance. They occur on relict, current-swept portions of the shelf and may be as old as Miocene in age (O'Brien et al. 1990). Younger (Pleistocene-Recent; "Type I") nodules occur in glauconitic foraminiferal sands on the upper slope, and are fairly small (<5 cm), earthy and friable, and range in color from yellow brown to light gray. In the terminology of Garri-

son & Kastner (1990; see above), the Neogene nodules are ferruginous D-phosphates while the younger nodules are F-phosphates (compare with Fig. 2).

The modern phosphorite nodules of East Australia are forming within the upper 20 cm of the sediments in association with the oxic/anoxic interface. P enrichments in pore waters is attributed to the reduction of iron oxyhydroxides, which release both phosphorus and iron (Marshall 1983; cf. Stumm & Leckie 1970, Krom & Berner 1981, Filipek & Owen 1981). Following this release, the iron and phosphorus can be incorporated into glauconite and CFA, respectively. This process is apparently maintained as a kind of "iron pumping" mechanism (e. g. Fig. 6), where any reduced (and thus solubilized) iron fluxes back to the sea floor where it may again be oxidized and become insoluble, adsorb phosphorus and return to the sediments with burial (see detailed discussions in O'Brien et al. 1990, Heggie et al. 1990). In this way, phosphorus input may become partly decoupled from organic matter in the near surface sediments and linked to the redox cycle of iron (cf. Shaffer 1986). O'Brien et al. (1987) also showed that the apatite and iron hydroxide content of the nodules are a function of their residence time within the upper 20 cm of the sediment column; nodules with long durations within this shallow zone rapidly accumulate both apatite and iron oxyhydroxide, whereas those buried soon after formation gain little of either phase.

#### Similarities between peruvian and East Australian phosphorites

It is interesting to conclude that although the physical oceanography off the coasts of Peru and East Australia are vastly different, both settings appear to record many similarities with respect to the precipitation of CFA. In both, the precipitation of CFA appears to be strongly linked to the sediment-water interface, rather than being driven by diagenesis of organic matter deep within the sedimentary pile. Glauconite is conspicuous in both settings. Organic carbon is abundant in sediments off Peru and lean in sediments off East Australia, partly because of the enhanced upwelling and high rates of primary productivity off Peru and partly because of very efficient bacterial utilization of sedimentary organic matter off East Australia; this efficient utilization is enhanced by a combination of very low sediment rates and strong sediment reworking, leading to a long residence time in the mixed layer (Moriarty et al. 1991, G.W. O'Brien, pers. comm.). In addition, it has been suggested for both settings that in order to develop and maintain high-grade quantities of phosphorite, the continual or sporadic precipitation of CFA must somehow be maintained over thousands of years in the interfacial zone optimal for its precipitation. Off Peru, such maintenance is likely due to bottom currents (e. g. Glenn & Arthur 1988, Glenn et al. 1994). Off Australia, such maintenance may be due to either bioturbation or currents (e. g. Heggie et al. 1990, O'Brien et al. 1990).

#### Ancient phosphorites

In addition to the wealth of information provided by recent studies of modern occurrences, much of what we know about phosphorites stems from study of the granular deposits which dominate the ancient record. Many of these deposits are quite large (which we term "giant phosphorites"), their distribution in the Phanerozoic is episodic (Fig. 7; see tabulation summary of Cook & McElhinny 1979), and most were deposited beneath rela-

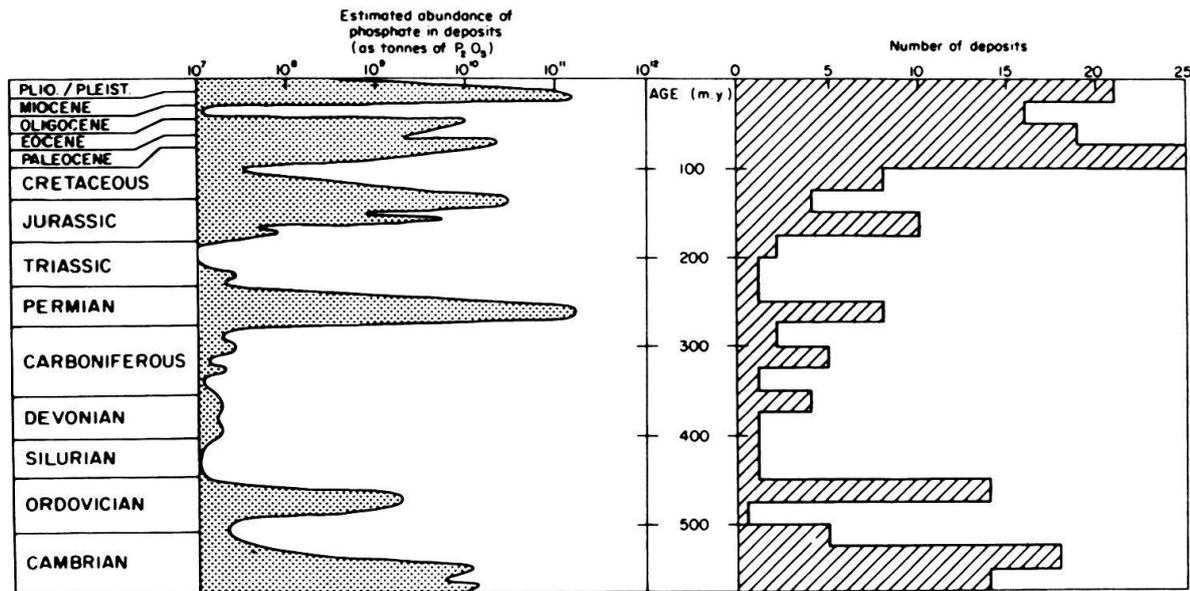
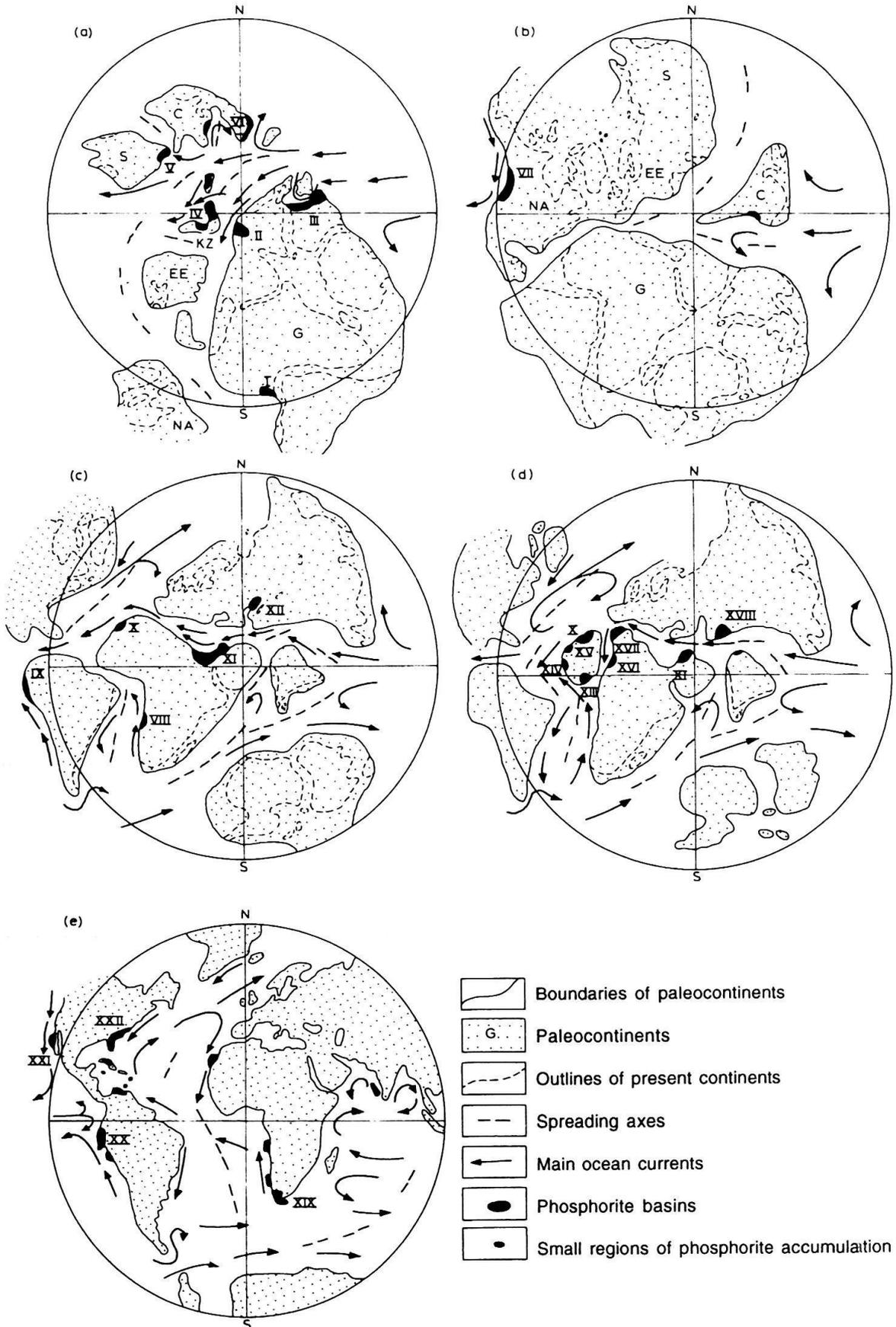


Fig. 7. Estimated abundance in metric tons of  $P_2O_5$  and number of phosphorite deposits through the Phanerozoic. The fixed time interval of the histogram is 25 m.y. A logarithmic scale is used for  $P_2O_5$  abundance. Regions with very large deposits are: Cambrian = Karatau, Russia, Georgina Basin, Central and SE China, Vietnam, Chub Sugal; Ordovician = Tennessee, Baltic area; Permian = W. USA; Jurassic = Russia; Upper Cretaceous = W. Africa, N. Africa, Mid. East; Miocene-Pliocene = SE USA. Many other smaller occurrences also occur within these time windows. From Cook & McElhinny 1979.

tively shallow waters of marginal seas and epeiric platforms (Fig. 8). Below, we highlight their relation to sea level change, sequence condensation, sequence stratigraphy, nutrient sources and aspects of their paleoenvironmental settings.

#### *Sea level and transgressions*

The idea that phosphorite genesis is linked to changes in sea level is not new. Major phosphorite deposition appears to correlate in a general way with elevated sea levels and, more specifically, with marine transgressions (Fig. 9; also see e. g. McKelvey et al. 1953, 1959, Cressman & Swanson 1964, Arthur & Jenkyns 1981, Riggs & Sheldon 1990, Glenn & Arthur 1990, Föllmi 1990, Herbig & Trappe, in press). This relationship appears to stem from the following interrelated factors: (1) Elevated sea levels expand the potential for suitable sites of phosphorite accumulation on shelves and in continental interiors; (2) elevated sea levels may allow for increased potential for upwelling into shelf seas; (3) transgressive episodes may favor phosphorite accumulation by restricting the locus of diluting siliciclastics in the landward direction (sediment starvation); (4) wave-induced and other cross-shelf currents may develop along flooded margins and platforms that aid to winnow, rework and concentrate authigenic precipitates into large deposits (sequence condensation). However, in addition to transgressive phases, it has also been suggested that lowering wave bases during relative falls of sea level may aid in reworking and concentrating phosphorite and other authigenic grains (Baturin 1971, 1981, Glenn & Arthur 1988, Grimm 1992).



*Phosphorites, condensed sections and sequence stratigraphy*

Condensed sections or sequences are of significance and interest because they represent a process of extremely slow net sedimentation over long periods of time. Such intervals have been long recognized to be characterized by the following features: (1) enrichment of well preserved fossils and fossil fragments, (2) faunal mixing, fossils from different paleontological zones within a single bed and (3) widespread distribution of sediments with negligible thicknesses. In addition, it has become increasingly recognized that intervals of stratigraphic condensation are also frequently marked by the occurrence of authigenic minerals, including phosphorites and glauconites. Of continuing debate, however, is the role with which sediment reworking and winnowing contributes to the condensation process (cf. Jenkyns 1971, Kennedy & Garrison 1975, Krajewski 1984, Kidwell 1989, Glenn & Arthur 1988, 1990, Glenn et al. 1988, Burnett et al. 1988, Föllmi 1990, O'Brien et al. 1990, Snyder et al. 1990).

With the advent of "sequence stratigraphy", condensed sections have taken on new meaning and significance as an integral component in the stratigraphic architecture of sequences controlled by fluctuations in relative sea level (e. g. Jervy 1988, Posamentier et al. 1988, Posamentier & Vail 1988). Loutit et al. (1988) and their colleagues define condensed sections in light of sequence stratigraphy as thin marine units of pelagic to hemipelagic sediments that: (1) are characterized by very low sedimentation rates that are aerially most extensive at the time of maximum transgression and coincident with the surface of maximum flooding, (2) are associated with apparent marine hiatuses and (3) occur as omission surfaces or marine hardgrounds. They result from sediment starvation during times of maximum rates of sea level rise. These occur along the break separating transgressive and highstand systems tracts (Fig. 10). Assuming that seismic reflectors reflect time-lines (Jervy 1988, Posamentier et al. 1988, Posamentier & Vail 1988), sequence condensation may, hypothetically, also occur anywhere that reflectors converge such as, for example, along surfaces on onlap, backstepping, downlap and toplap (Kidwell 1991, Fig. 10). In addition, while phosphorites may be generally associated with transgressive phases of second and third orders changes of sea level (5–50 and 0.5–5 Ma, respectively), much reworking of these may occur during intervening higher orders of sea level change (fourth, fifth and sixth order; 0.1–0.5, 0.01–0.1 and <0.01 Ma, respectively). However, as noted above, most major episodes of phosphorite genesis do appear to be related to transgressive phases, although the occurrence of reworked deposits within the upper portions of highstand systems tracts may also reflect episodes of condensation and bypassing that occur in association with the convergence of toplapping seismic reflectors (Fig. 10). In sum, the actual distribution of condensed deposits within seismic sequences is prob-

Fig. 8. Continents and oceans of the main episodes of phosphorite formation of the Phanerozoic. Episodes: (a) Early Cambrian; (b) Early Permian; (c) Late Cretaceous; (d) Paleocene/Eocene; (e) Neogene. Legend: 1 = boundaries of paleocontinents; 2 = paleocontinents (G = Gondwana, C = Chinese, S = Siberian, KZ = Kazakhstan, EE = East European, NA = North American); 3 = outlines of present continents; 4 = spreading axes; 5 = main ocean currents; 6 = phosphorite basins (I = Pendjari, II = Udaipur, III = Georgia, IV = Karatau, V = Höbsögöl, VI = South Chinese, VII = Rocky Mountains, VIII = Congo, IX = East Cordilleran, X = Moroccan, XI = East Mediterranean, XII = Aktyubinsk, XIII = Togo-Nigerian, XIV = Senegal, XV = West Saharan, XVI = Mali-Nigerian, XVII = Algerian-Tunisian, XVIII = Central Asian, XIX = Agulhas, XX = Sechura, XXI = Californian, XXII = Atlantic Coastal Plain); 7 = small regions of phosphorite accumulation. From Baturin 1981 (slightly rearranged), reprinted with permission of Elsevier Science.

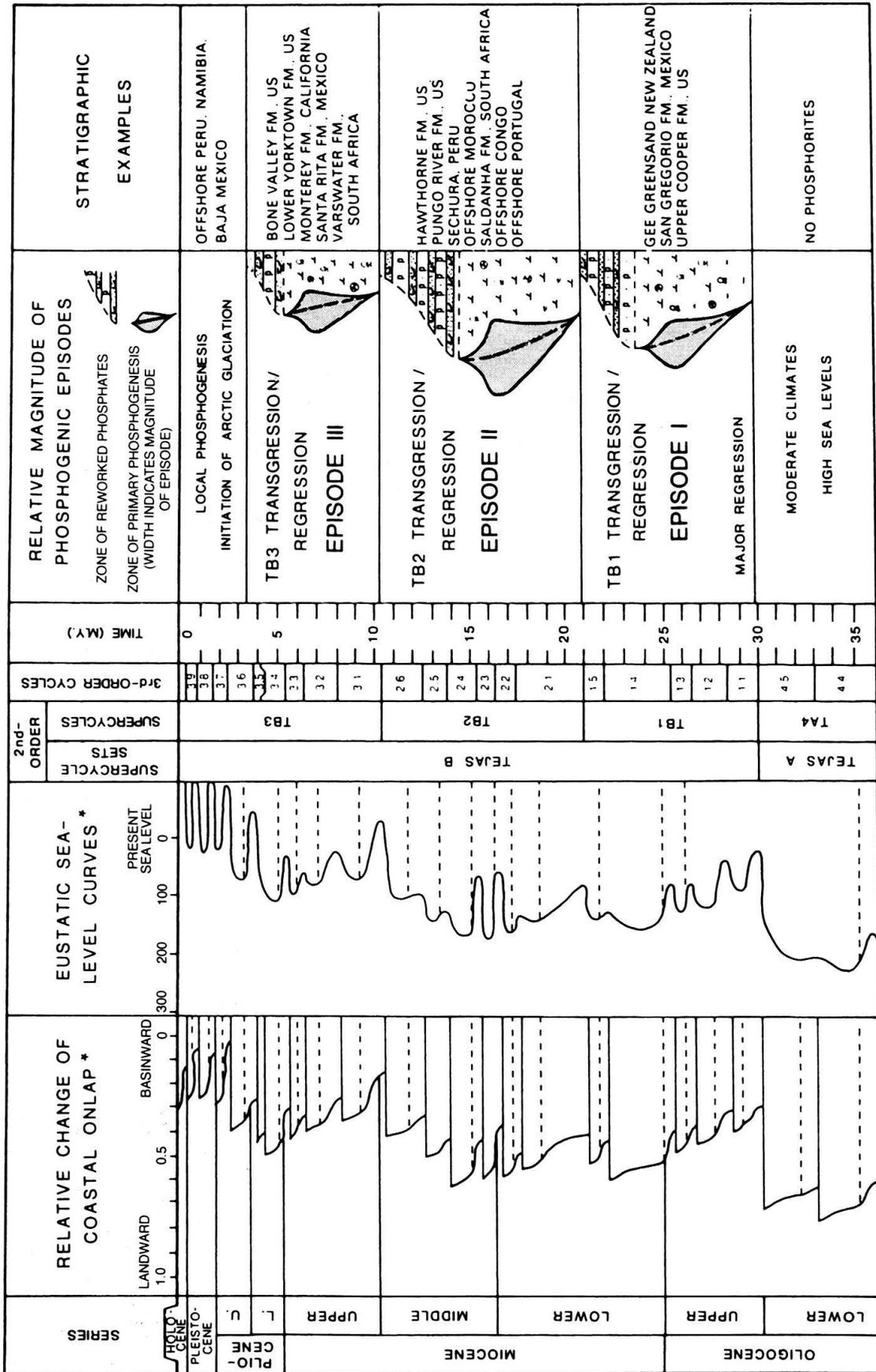


Fig. 9. Comparison of Upper Cenozoic phosphorite depositional episodes with second- and third-order curves of coastal onlap and eustatic sea-level events of Haq et al. (1987). From Riggs & Sheldon (1990). © Cambridge University Press, reprinted with the permission of Cambridge University Press.

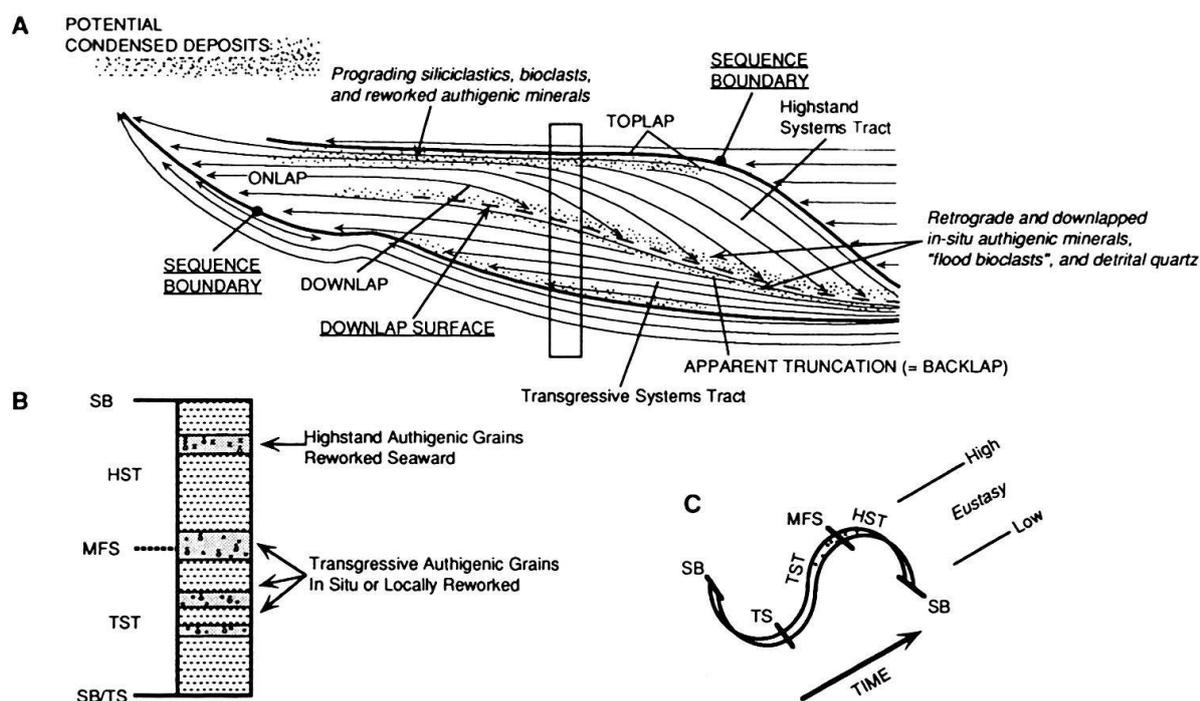


Fig. 10. Potential relationships between sequence stratigraphy, condensed sections and phosphorites. (A) Possible positions of sequence condensation within an idealized depositional sequence (stipples), (after Kidwell 1991). (B) Schematic illustration of the placement of non-reworked pristine authigenic phosphorite (and/or glauconite) and reworked phosphorite (and/or glauconite). Pristine phosphates may form within transgressive systems tracts and at the maximum flooding surface, whereas later phases are reworked seaward within highstand systems tracts. (C) The timing of systems tracts development with respect to one cycle of sea level change. LST = lowstand systems tract, TST = transgressive systems tract, HST = highstand systems tract, TS = transgressive surface, MFS = maximum flooding surface, SB = sequence boundary. Dots on the sea level curve represent locations of maximum phosphorite emplacement. After Glenn & Kronen 1993.

ably more complex than depicted by recent models. Still, studies which have attempted to understand the origin of phosphorites (and glauconites) within the context of sequence stratigraphic models remain relatively few (Glenn 1990a, Glenn & Arthur 1990, Southgate & Shergold 1991, Riggs et al. 1990, Snyder et al. 1990, Föllmi et al. 1992, Garrison 1992a, Grim 1992, Glenn et al. 1993).

### *Phosphorite giants: Assessments and remaining questions*

Large phosphorite deposits, such as those in the Cretaceous Tethyan deposits and the Permian Phosphoria Formation of western North America, have been widely attributed to extremes in oceanic/climatic conditions, causing apparently accelerated P withdrawal from the ocean into shelf, slope and epicontinental sediments (Sheldon 1980, 1981, cf. Cook & McElhenny 1979, Arthur & Jenkins 1981). The episodic character of phosphorite giant deposition through the Phanerozoic has spawned postulates that these were times of globally equable warm climates ("polytaxic episodes") during which deep sea waters became enriched in dissolved phosphorus (Fischer & Arthur 1977), times when continents drifted into low latitude locations during particular phases of continental dispersal favorable to upwelling (Cook & McElhenny 1979), times of continental glaciation and global cooling

when increased vertical oceanic overturn releases phosphorus previously housed in the deep sea (Sheldon 1980, Cook & Cook 1985), and times of transgression coupled with warm global temperatures, consequent increased chemical weathering, and the development of widespread oxygen-depleted waters (Arthur & Jenkyns 1981). None of the mechanisms work perfectly and each episode has its own particularities. Further investigations will be required to determine whether a phosphorite giant records anomalously large episodes of net P burial over geologic time spans (and thus large increases in weathering-delivered supply of P to the oceans; cf. Arthur & Jenkyns 1981, Barron & Frakes 1990, Compton et al. 1990, 1993, Föllmi et al. 1993, Delaney & Filippelli 1994). In addition, is it possible that global P burial rates have been relatively constant over geological time and the non-uniform occurrence of phosphorite giants accounts only for the presence of buried apatite in a conspicuous and concentrated state, rather than broadly disseminated?

Phosphorite giants appear to record extremes in the geographic localization and hydraulic concentration of disseminated apatite into thick, laterally extensive and economic phosphorite. New studies of the Peru shelf and slope (Glenn et al. 1994), however, suggest that the amount of phosphorite forming today, mainly as phosphorite hardgrounds over hundreds of thousands of years, may actually be larger than some of the classic granular phosphorite giants that crop out on land. In addition, other recent calculations suggest that several phosphorite giants required a net P withdrawal rate that was comparable to that seen in modern Peru margin muds (Filippelli & Delaney 1992). Thus, if there is, in fact, an episodicity to the anomalous development of large phosphorites through time (Fig. 7), it is becoming increasingly apparent that the present day may have to be included as one of these anomalies.

Comparison with modern phosphorite occurrences has led many workers to conclude that most if not all ancient phosphorite giants were laid down beneath upwelling depocenters. This has remained a particularly attractive scenario, especially for deposits that developed, as today, along western continental margins (e. g. Permian Phosphoria Formation; Miocene Monterey Formation of California, Caleta Herradura Formation of Chile and Sechura phosphorites of Peru). In addition, the extensive Miocene phosphorites of the southeast U.S. have also been linked to obstruction-related upwelling of the Gulf Stream western boundary current (e. g. Riggs 1984, Snyder et al. 1990). Does the co-eval occurrence of several large Late Cretaceous phosphorite deposits along southern Tethys (Egypt, Israel, Jordan, Syria, Turkey, Iran) also demand that a continental margin upwelling scenario be invoked? Sheldon (1980) suggested that upwelled equatorial divergence waters from the east were advected westward along the submerged Middle East-North African cratonic margin. Others (Glenn & Mansour 1979, Ganz 1984, Germann et al. 1985, Reiss 1988, Abed 1994, Kolodny & Garrison 1994) have suggested upwelling of waters derived from the Tethyan trough to the north; the paleolatitude of the region was 8°–15°N and easterly winds may have caused northward-directed Ekman transport of surface waters with consequent upwelling of deeper waters. Yet, Glenn & Arthur (1988) stressed that upwelled waters are rapidly depleted of nutrients, that productivity is greatly diminished within relatively short distances of the locus of upwelling, and that some of the Tethyan deposits were laid down beneath relatively shallow waters that were apparently tens to hundreds of kilometers removed from the open Tethyan margin to the north. They questioned whether it is not also possible that a common link for these occurrences was the delivery of fluvial-borne P derived from deeply weathered hinterlands to the south (Glenn & Arthur 1990,

Glenn et al. 1994), an idea now known to have been proposed earlier by Russian investigators (Mikhailov et al. 1972). Could inputs of phosphorus bound to iron compounds (Fig. 1; the Fe-P model of Glenn & Arthur 1990) help explain the co-existence of phosphorites, iron phosphorites and iron-rich glauconites in these and other settings? Indeed, many important questions remain, not only about the precise mechanism whereby phosphorus is transferred into sediments, but also about the ultimate delivery mechanism of phosphorus to eventual sites of "giant" accumulation. Insights into the phosphorite giant province of the Cretaceous southern Tethys and elsewhere will require expanded commitment to international cooperation and objective collaborative investigation.

#### *Paleoenvironmental impacts of phosphogenesis*

One of the more severe environmental problems mankind is presently confronted with is the anthropogenic fertilization and eutrophication of increasingly large ecological systems. The rising demand for phosphate and nitrate in agriculture, industry and household in the last 150 years has provoked an accelerated spreading of these compounds in the natural environment. Excess nutrient loading profoundly changes ecological systems involved (see also Jarvis et al. 1994). Lakes adjacent to heavily populated centers or intensively utilized agricultural areas show substantial increases in the standing stock of green algae and fish. Oxygen demand for decomposition of the algal organic matter may exceed available levels and seasonal or stable dysaerobic or anaerobic bottom water conditions may develop. This, in turn, severely affects present benthic lake communities. Similar changes in ecosystems are observed in semi-enclosed peripheral seas such as the Baltic Sea, the North Sea, the Black Sea and Santa Barbara Basin (e. g. Baden et al. 1990). In tropical reef systems, increased nutrient levels may be one of the causes of the observed widespread decoupling of symbiotic zooxanthellids from their coral hosts and consequent reef deterioration and breakdown ("coral bleaching", e. g. Flanagan 1993, also see Hallock & Schlager 1986).

The principal process through which eutrophication is coupled with environmental change is photosynthesis. Phosphate and nitrate are essential nutrients and fuel photoautotrophs. In a Redfield-type situation of P-limitation, each phosphorus atom may drive the transformation of as much as 106 inorganic carbon atoms into organic ones. In terrestrial environments, this ratio may even be higher (up to 800; Berner et al. 1993). The amount of available nutrients per time unit influences not only the quantity of photoautotrophs (and therefore of organic matter), but also their composition. For instance, opportunistic, fast growing and reproducing, photoautotrophs such as certain siliceous algae prevail in nutrient-rich environments. The amount of organic matter produced per time unit, in turn, is decisive for the oxygen demand below the zone of primary productivity, for the presence and composition of the subjacent benthic community, and for the amount of organic matter sequestered in the sediments (e. g. Pedersen & Calvert 1990).

With the environmental impact of present-day anthropogenic nutrient loading becoming increasingly evident, we may ask if natural fluctuations in nutrients have affected ancient ecosystems as well? In other words, do we see temporal coincidences of ecological change with changes of global nutrient cycles in the sedimentary record? Here, phosphorus may be a more appropriate tracer than nitrate, because, in its inorganic form, once stored in the sediments, it behaves in a relatively conservative way (e. g. Berner et

al. 1993). It may also be the limiting nutrient in large parts of the biosphere (e. g. Mackenzie et al. 1993). Good recorders of environmental change are any kind of fossiliferous sediments, which are relatively continuous over representative time spans. Pelagic sediments may have an advantage in being a potential carrier of additional chemical and isotopic information relevant to environmental change (e. g. Sr or stable isotopes of whole rock or selected organisms).

In the following, we briefly discuss a case example that demonstrates a possible link between phosphorus loading, and ecological and environmental change (cf. Föllmi et al. 1993, 1994). In the latest-most Jurassic and early Cretaceous, a shallow-water carbonate platform developed along the northern Tethyan margin. In outcrops of the northern Alps in eastern Switzerland and western Austria, this platform system exhibits three different evolutionary stages, which repeatedly occurred:

1. A carbonate-platform buildup dominated of reef-type organisms such as chaetids, stromatoporoids, corals and rudists. Oolites are important constituents as well. In this mode, siliciclastics and preserved biogenic silica are very rare ("coral-oolite carbonate-production mode"; late Tithonian to early Valanginian and early Barremian to early Aptian).
2. A carbonate-platform buildup dominated by the remains of crinoids. Bryozoans, thick shelly bivalves, brachiopods and sponge spicules are additional faunal elements of relative importance. Reef-type organisms are lacking. Oolites only appear in subordinate quantities and may have been reworked from carbonates produced in the coral-oolite mode. Siliciclastics are common and cherts are frequently observed ("crinoid-bryozoan carbonate-production mode"; early Valanginian, early to late Hauterivian and late Aptian).
3. The formation of thin and highly condensed phosphate-rich crusts and horizons, which lasted up to several million years. Their formation was accompanied by physical and biological erosion in large areas of the platform and a pronounced sea-level rise. These phases have been identified as periods of (incipient) platform drowning (Schlager 1989) ("platform destruction, condensation and phosphogenesis mode"; early Valanginian to early Hauterivian, middle Hauterivian, late Hauterivian to early Barremian, early Aptian to early late Aptian and latest Aptian to earliest Albian).

In using an actualistic approach, the coral-oolite carbonate-production mode may have been associated with warm and transparent, oligotrophic waters. On the other hand, the crinoid-bryozoan mode may be attributable to deposition in mesotrophic waters, as is indicated by the dominance of crinoids (a fast-growing and versatile group of organisms well adapted to filter suspended organic matter out of the water column) and the presence of siliciclastics and chert nodules (including sponge spicules and radiolarians). The mode of platform destruction, condensation and phosphogenesis is thought to be indicative of eutrophic conditions, which severely limited growth and spreading of the benthic carbonate-producing organisms (Föllmi et al. 1994). Shifts between these three modes, i. e., between different ecological systems dominating the platform and determining rate and mode of platform accumulation (and erosion), were likely driven by changes in nutrient and especially phosphorus levels in the surrounding bottom waters. Changes in nutrient inventory, in turn, appears to be related to the presence and quantities of siliciclastics and, for this reason, to continental weathering (e. g. Weissert 1990).

An excellent indication that this postulated relation between nutrients and ecological change in the evolution of the early Cretaceous platform is embedded in global change is given with the good temporal correlation between the drowning episodes and positive excursions in the  $\delta^{13}\text{C}$  record. These positive excursions are established in pelagic sediments of the southern Alps and Appennines and have been confirmed for the Valanginian and late Aptian in outer-shelf, hemipelagic, successions deposited beyond the here-described platform system (Fig. 11; Weissert & Lini 1991, Lini et al. 1992, Föllmi et al. 1994). The good fit between the platform-drowning episodes coupled with phosphogenesis and the positive excursions in the pelagic  $\delta^{13}\text{C}$  record may indicate that an underlying, global, mechanism was responsible for the observed changes in ecology and inferred changes in nutrient levels. This mechanism induced high nutrient levels, probably coupled with increased continental weathering rates and increased input of siliciclastics, a sea-level rise and an accelerated carbon cycle with increased burial rates of organic carbon as manifested by the positive excursions in the  $\delta^{13}\text{C}$  record. Weissert (1990), Weissert & Lini (1991) and Föllmi et al. (1993, 1994) identified reinforced greenhouse conditions as a possible candidate for inducing this chain of events.

The question that remains to be answered is in how far the above can be tested in independent localities. A similar correlation between an episode of phosphogenesis and a pronounced excursion in the  $\delta^{13}\text{C}$  record has been proposed for the early middle Miocene (Vincent & Berger 1985, Compton et al. 1990, 1993). In taking the Cretaceous and Tertiary pelagic record for background phosphate levels compiled by Cook (1984) for the Indian Ocean, we see a fairly good fit between increased phosphate burial rates and positive  $\delta^{13}\text{C}$  excursions, especially for the Tertiary (Föllmi 1993, Föllmi et al. 1993). This all, however, remains tentative, if a better approximation for global behavior of the phosphorus cycle in the geological past cannot be found. A promising approach in this direction is being taken by Filippelli & Delaney (1994b), who are systematically measuring and comparing background phosphate contents in different settings of phosphogenesis.

## Conclusions

The above discussions have highlighted some of the salient aspects of what is known and unknown about the sedimentology of phosphorites. We have emphasized that despite the "modern" textbook view of marine phosphorites, phosphatic sediments form not only beneath upwelling systems, but also on oceanic islands, atop seamounts, guyots and plateaus and on shelves, slopes and in epeiric environments that may not have experienced upwelling at all. There remains much controversy about the origin of many phosphorites and phosphatic sediments within all of these settings. We summarize several outstanding remaining questions about phosphorites below.

1. In view of the increase in the number of recent discoveries of modern phosphorites and the possibility of their apparently large overall extent, we have again to ask the old question of whether the ancient phosphorite giants represent periods of abnormal oceanography that marked deviations in the global cycling of phosphorus. Alternatively, because the geologic record of major phosphorite development does appear to be episodic, should the present ocean be considered as one of these episodes?

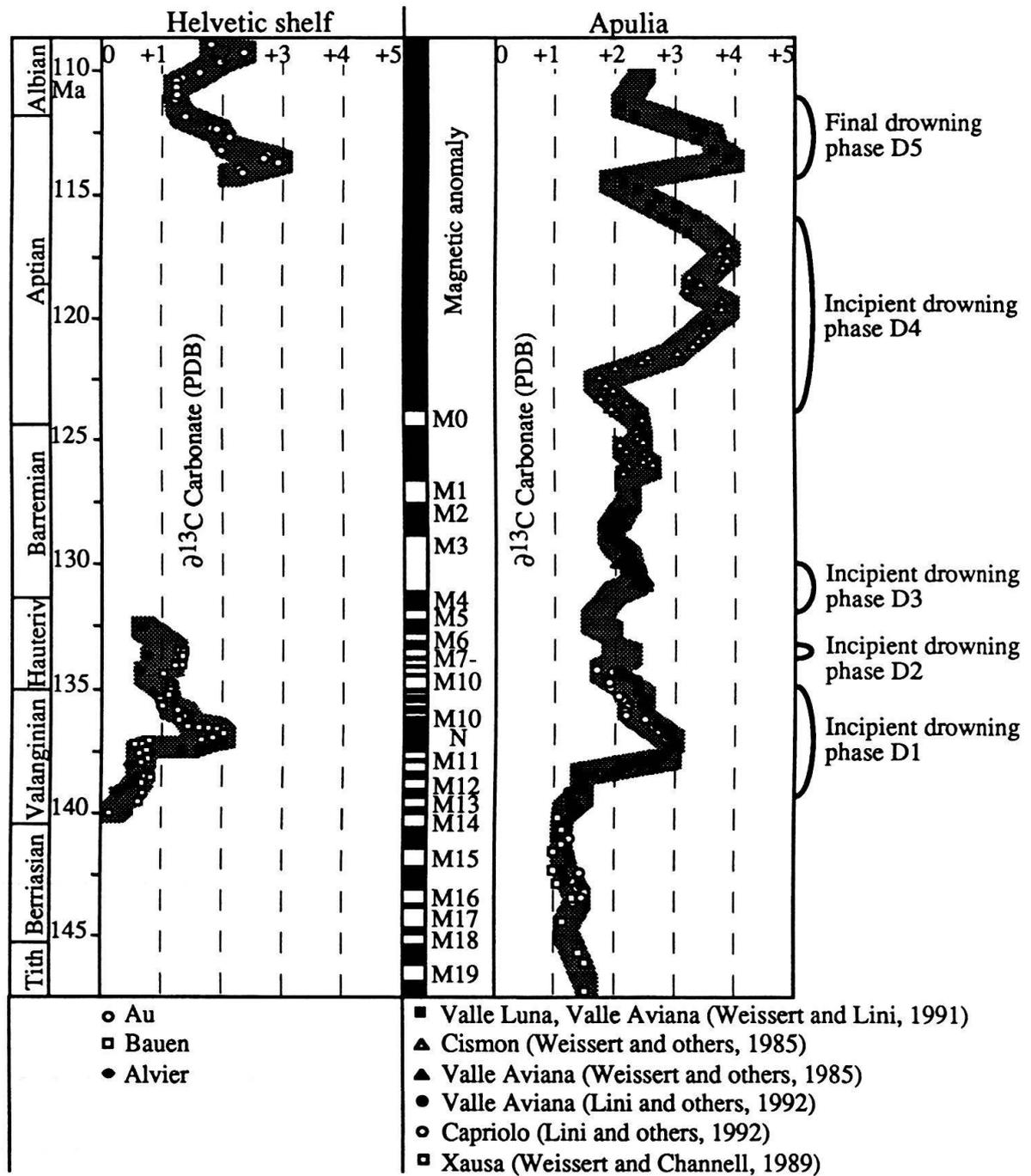


Fig. 11. Correlation of the early Cretaceous  $\delta^{13}\text{C}$  record from the pelagic realm (southern Alps and Apennines = Apulia) and the hemipelagic realm (northern tethyan margin = Helvetic shelf), and episodes of platform drowning and phosphogenesis in the northern tethyan shallow-water carbonate platform system (from Föllmi et al. 1994). Reprinted with permission of the Geol. Soc. of America.

2. The modern marine phosphorus cycle remains poorly understood and needs substantial refinement. Refined measurements of different types of phosphorus fluxes in all major oceanic settings are needed (i. e. sorbed P, Fe-bound P, CFA-P,  $\text{CaCO}_3$ -bound-P, biogenic-P, detrital apatite, organic P; see Ruttenberg 1992). Can carbonate fluor-

- apatite also form at deeper burial depths than that sampled by recent studies of modern CFA precipitation on the sea floor and, if so, how does this quantitatively effect our understanding of the global inventory and cycling of phosphorus?
3. Not all occurrences of phosphorite on oceanic islands appear to be the result of leaching guano. While this model is widely held, a puzzle remains as to why no bird bones have been found in any insular deposits and how such occurrences can occur in areas that are presently oligotrophic. Further study is needed of these occurrences in order to differentiate origins as different as guano, endo-upwelling and precipitation within insular marine lakes. Understanding the origin of associated dolomites in these deposits remains an important part of the puzzle. Understanding the relationship of insular occurrences to climatic variability also remains an important problem.
  4. The origin of phosphorites from seamounts and guyots and their relationship to Mn/Fe crust remains unresolved. Future studies are needed that tectonically back-track these occurrences to their paleoceanographic position. Age dating of these deposits remains a fundamental problem in phosphorite research, but one that may help in the potential utilization of such rocks as important recorders of past oceanic chemistry.
  5. There appears to be clear and ample sedimentology and geochemical evidence in support of the basic tenant of the "Baturin Model", which envisions the physical reworking of previously existing primary phosphates (washing, winnowing and concentration of phosphatic particles) to form granular phosphorites. Coarser grained, conglomeratic phosphorite hardgrounds may form in similar ways. How such reworking occurs and what exactly served as the pre-existing substrate, however, often remains a matter of conjecture and may be different in different settings. Only rarely has evidence for the parental ("pristine") sediment for the redeposited grains been found. Further assessment of the potential role of redeposition as sediment-gravity flows is also needed.
  6. Application of sequence stratigraphic models to the origin of phosphorites is needed.
  7. One extremely important aspect resulting from recent studies is that carbonate fluorapatite can and does form as an early diagenetic precipitate directly adjacent to the sea floor. If it forms at much deeper depths in the sediment pile, then it stands little chance of being reworked into granular lag deposits of economic worth. This seems to necessitate either rapid CFA growth (which often does not appear to be the case for crusts and nodules; see Kim & Burnett 1985, 1986), or some other mechanism, such as bioerosion or current sweeping, which can act to prolong the length of time that these phases reside at the sea floor. However, can granular phosphorite form *in situ* without significant reworking, as suggested by the recent growth estimates of pellets from the Peru margin (Burnett et al. 1988)?
  8. What is the origin of the interfacial spikes of phosphorus associated with phosphogenesis off Peru and Baja California? Are they the result of a processes of phosphorus generation that are detached from the suboxic to anoxic microbial degradation of organic matter? Do they represent a build-up of phosphorus-rich pore waters beneath newly forming CFA proto-crusts?
  9. Within the shallow portions of the sediment pile, what controls or limits deeper CFA precipitation (molecular diffusion? lattice poisoning? lack of appropriate bacteria? molecular complexation reactions?)?

10. A long-standing debate in phosphorite research which still demands answer is whether phosphate can precipitate directly above the sea floor, whether it be as hardgrounds or pavements, or as those mysterious little grains we call pellets. Hardgrounds and nodules of CFA may derive phosphorus from underlying sediments, but, in other cases, these phases appear to grow from within the sediments up toward the sediment-water interface (e. g. Kim & Burnett 1986, Glenn et al. 1988). Do open-ocean phosphorites derive their phosphorus supply directly from the water column?
11. What is the origin of coated grains and other phosphate pellets? It has been repeatedly suggested that coated pelletal grains must indicate precipitation on the sea floor (as phosphate oolites). The isotopic composition of identical grains from the Peru slope clearly suggests their diagenetic precipitation from pore waters. However, several of us have marveled at the fact that such grains also occur within insular "guano" phosphorite horizons, such as on Nauru. Why are such grains coated? Do bacteria play a role? Whether other ancient coated grains have formed as true ooids, on a gently agitated sea floor that is saturated with respect to CFA, remains unresolved.
12. Bentor (1980) and numerous others have stated that modern phosphorite occurrences are poor analogs for ancient deposits because the modern did not contain phosphorite pellets and were dominated by phosphorite nodules, whereas the ancient deposits were dominated by pelletal (granular) phosphorites. Today, this assessment appears to ring only partially true. Recent studies have now demonstrated that pellet phosphorite does occur in the modern setting, and many phosphorite hardgrounds may go relatively undetected within some ancient phosphorite suites. Still, the ancient suites do appear to be dominated by pelletal phosphorites, and the modern by hardgrounds. What is the reason for this difference?
13. What is the ultimate source of phosphorus for giant continental margin and epeiric sea occurrences? Are all these a indirect product of upwelling, or can some have received more direct fluvial phosphorus supplies?

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