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The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits

K.B. Föllmi

Geological Institute, ETH-Zentrum, CH-8092 Zürich, Switzerland

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Abstract

Phosphorus (in the form of phosphate) is an essential nutrient and energy carrier on many different levels of life, and a key element in mediating between living and lifeless parts of the biosphere. One of the most important aspects of the phosphorus cycle is its vital role in governing productivity, thereby interacting with the exogenic part of the carbon cycle, which, in turn, is important in regulating Earth's climate.

Phosphorus is a prime element to be traced in Earth's history, because it allows for the reconstruction of long-term feedback mechanisms between climate, environment and ecology, and of global change as such. Marine sedimentary phosphate deposits are particularly suited to study aspects of the phosphorus cycle, because, in the case of ubiquity, their origin may result from a general acceleration of the global phosphorus cycle. Sources of sedimentary phosphate are microbial breakdown of buried organic matter and redox-driven phosphate desorption from iron and manganese oxyhydroxides. Dissolved sea-water phosphate represents an additional source which may become important in the formation of phosphatic hardgrounds. The main locus of phosphogenesis is near the sediment–water interface, but phosphogenesis also occurs at greater sediment depths. Current-induced winnowing and transport processes along the sea floor concentrate phosphate precipitates into deposits, which exhibit internal stratification patterns typical for the prevailing hydraulic energy regime. In a sequence-stratigraphic context, phosphate deposits preferentially occur along marine or maximum flooding surfaces. Consequent sedimentary reworking may result in the transfer of phosphates to highstand or lowstand deposits.

(Bio-)chemical weathering on continents represents the most significant source of bioavailable phosphorus. This implies that long-term changes in marine phosphorus levels — and with these changes in marine ecology, productivity rates and ratios of exported carbonate carbon and organic carbon — are a response to changes in continental weathering rates. A compilation of marine sedimentary phosphorus burial rates for the last 160 Myr suggests that natural variations have occurred that span one order of magnitude. For the late Jurassic, Cretaceous and most of the Paleogene, the phosphorus cycle appears to have been accelerated in times of climate warming, which was most likely due to the spreading of zones of humid climate and more intense continental weathering. In the Neogene, the phosphorus cycle appears to have responded to changes in glacially induced weathering. This suggests that uniform interpretations with respect to the emplacement of major phosphorite deposits should be treated with caution. Integrated analyses of the sedimentary and biogeochemical context of phosphorite occurrences may help to identify paleoenvironmental conditions, as well as to improve our understanding of periods of enhanced phosphate accumulation, periods which were usually characterized by steep gradients in the development of climate and environment.

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With regard to the complexity of feedback mechanisms between the phosphorus cycle and the biosphere, the present-day input rates of phosphate into the world's oceans should be of great concern. They are more than doubled by anthropogenic means and affect ecological systems on a rapidly increasing scale.

"*In all these various formations our coprolites form records of warfare, waged by successive generations of inhabitants of our planet on one another: the imperishable phosphate of lime, derived from their digested skeletons, has become embalmed in the substance and foundations of the everlasting hills; and the general law of Nature which bids all to eat and be eaten in their turn, upon our globe; the carnivores in each period of the world's history fulfilling their destiny office, – to check excess progress of life, and maintain the balance of creation*" (Buckland, 1835, p. 235)

"*Organic remains must sometimes accumulate in vast numbers on the sea-bed, and sometimes be buried in the sediments; it seems to us that the decomposition of such organic remains is the immediate source of the phosphates in the concretions here described*" (Murray and Renard, 1891, p. 398)

"*The great majority of the bedded phosphate deposits of all geological horizons occur along a plane of disconformity, and as a rule in association with calcareous bedrock, which is often secondarily phosphatized. This points to concentration of phosphatic material originally scattered widely through the missing formation*" (Grabau, 1919, p. 104)

1. Introduction

1.1. A historical overview

In his book *Historia Inventionis Phosphori*, G.W. Leibniz (1646–1716) described the discovery of the element phosphorus. He stated that, around 1669, the Hamburg alchemist and merchant H. Brand extracted phosphorus "from the spirit of urine", while he was searching for the philosopher's stone. By heating white sand mixed with evaporited urine, he obtained a white solid that glowed in the dark and ignited spontaneously in the air. In 1771, J.G. Gahn and C.W. Scheele isolated phosphorus in larger quantities by heating bone ash mixed with carbon and sand. In spite of different trials to apply phosphorus in an array of medical treatments, not much more became known about phosphorus for the next 135 years, until the year 1906, when H. Harden and W.J. Young discovered the properties of phosphorus as an essential nutrient in the fermentation of sugar in yeast (Degens, 1989). Soon afterwards, recognition followed of the central role of phosphorus in energy transfer processes on all levels in living systems and of the vital property of phosphorus (in the form of phosphate) as an essential nutrient in the biosphere.

First descriptions of occurrences of marine phosphorites emerged in the 18th century, and the first detailed account of phosphate-rich sediments was published by W.Buckland (1835; see quotation). In 1838 or 1839, W. Buckland showed the Liassic phosphorite occurrences of southern England to J. Liebig, a German chemist, who soon afterwards suggested that phosphorites could be used as fertilizer. In 1842, J. Lawes developed a method of producing a soluble fertilizer through the dissolution of phosphorite in H_2SO_4 (a method still widely used in the phosphate exploitation industry). This discovery led to the beginning of widespread exploration and exploitation of phosphorites. In the following years, phosphorite occurrences were discovered and described from different localities in the United Kingdom, from Belgium, France, Algeria, Tunisia, Central Russia, South and North Carolina, Florida and eastern Canada (Cook et al., 1990).

The first recovery of offshore marine phosphorites occurred during the famous expedition of the H.M.S. *Challenger* (1873–1876), with the dredging of phosphatized nodules and pebbles from the Agulhas bank offshore South Africa. Murray and Renard (1891; see quotation) described this occurrence and related the origin of phosphatic nodules in general to episodes of mass mortality and the subsequent release of phosphates from decaying organic matter. According to these authors, mass mortality was brought about by the interference of cold and warm water currents (compare also Collet, 1906; Heim and Seitz, 1934; Brongersma-Sanders, 1957; Sheldon, 1981). In 1919, A. Grabau stressed the importance of the prevalent coincidence of phosphatic sediments and stratigraphic unconformities (see quotation). He drew attention to the concept that reworking processes are agents responsible for the formation of macroscopic sedimentary phosphate accumulations (Grabau, 1919; compare also Heim, 1934; Schaub, 1936, Schaub, 1948; Kennedy and Garrison, 1975). These mechanisms, alluded to in the early days of sedimentology, have been discussed in later works. The effect of mass mortality and its feasibility as a source of phosphate trapped in phosphatic deposits was questioned by Blackwelder (1916) (compare also Dietz et al., 1942; Brongersma-Sanders, 1957). The importance of interfering cold and warm water currents was reinterpreted in the classical work of Kasakov (1937) in terms of dynamic coastal upwelling mechanisms. Furthermore, A. Kasakov proposed that phosphate may directly precipitate from upwelling seawater. Discussions on the importance of sediment reworking in processes of phosphate concentration and condensation were conducted, for instance, by Heim (1934; in Heim and Seitz, 1934) and Schaub (1936, Schaub (1948). Many elements of the ideas brought forward in the first half of this century, however, are still valid, as will be shown in the following chapters.

In the last four decades, our understanding of the phosphorus cycle and its interaction with the environment has considerably grown (e.g., Cook et al., 1990). This stems from intensive studies on the Phosphoria Formation by representatives of the U.S. Geological Survey (e.g., McKelvey et al., 1959) and on other continental outcrops (e.g., Kennedy and Garrison, 1975; Riggs, 1979; Jarvis, 1980, Jarvis, 1992; Krajewski, 1984; Southgate, 1986; Garrison et al., 1987, Garrison et al., 1990; Prévôt, 1990; Glenn and Arthur, 1990), from experimental work (e.g., Ames, 1959; McConnell, 1965; Gulbrandsen, 1969; Nathan and Lucas, 1976; Atlas and Pytkowicz, 1977; Lucas and Prévôt, 1981, Lucas and Prévôt, 1984, Lucas and Prévôt, 1985; Prévôt et al., 1989; Jahnke, 1984; Van Cappellen and Berner, 1988; Van Cappellen, 1991), and last but certainly not least, from observations on offshore, marine, deposits (e.g., Baturin, 1971a, Baturin, 1982; Von der Borch, 1970; Manheim et al., 1975, Manheim et al., 1980; Burnett, 1977; Froelich et al., 1988; Glenn and Arthur, 1988; Ruttenberg and Berner, 1993).

1.2. Importance of phoshorus

Phosphorus, i.e., $\phi\omega\sigma\phi o\rho o\sigma$, literally means "carrier of light", a connotation related to the capacity of phosphorus to ignite when exposed to air and to luminescence ("phosphorescence") in the dark (Degens, 1989). Phosphorus owes its name and uniqueness to its capacity to transfer energy on different levels in life and the biosphere (in the form of phosphate). This stems from the electron configuration, where one of the 3s or 3p electrons can be transferred to the 3d orbital. Due to this extra electron, phosphate (PO_4) structures are flexible, reactive, and can easily adopt to different structures and functions in living systems.

The properties of phosphorus as an energy carrier within life make this element to one of the most fundamental biophile elements in processes mediating between the living and lifeless parts of the biosphere. As an essential nutrient, phosphorus (in the form of phosphate) represents an important driving and regulating force behind biological productivity. Rates of productivity, in turn, determine the velocity with which atmospheric CO_2 is converted into organic matter, which is subsequently prone to storage in soils and sediments. This links the phosphorus cycle closely to the cycles of carbon and other biophile elements, such as oxygen, sulfur, nitrogen and iron, and provides phosphorus with extensive regulating capacities in processes such as climate, environmental and ecological change.

In spite of tremendous research efforts, many aspects of the global phosphorus cycle are still poorly understood and in need of further elucidation, especially in the light of the considerable anthropogenic increase in phosphate mobilization and flux rates. Phosphate flux rates have been more than doubled by human activity on a global scale (Froelich et al., 1982; Froelich, 1984; Caraco, 1993), and this may be beneficial in the short term (e.g., in the application of fertilizers), but is certainly negatively affecting the biosphere in the long term (e.g., through the alteration and devastation of benthic communities in freshwater and nearshore marine environments; Caraco, 1993). Furthermore, phosphate is probably already interfering with global climate by compensating for approximately 10% of the yearly increase in atmospheric CO_2 from anthropogenic sources (Mackenzie et al., 1993).

1.3. Present-day research, open questions

At the center of present-day research stands the study of transformation processes at critical interfaces of the phosphorus cycle. Topics here are mobilization and transformation processes of phosphate during continental weathering and soil formation, and storage processes of organic phosphate, both in natural as well as in experimental laboratories. A second interface of intense study is the continental–marine boundary. Here recent interests are directed towards the characterization of different phases of riverine phosphate, and of transformation and sedimentation processes of different phosphate phases in estuarine and deltaic settings. A third boundary which attracts major attention is the sediment–water interface and the transport and concentration processes across this important boundary. Here much research aims for a better understanding of microbiological and biogeochemical processes responsible for the precipitation of phosphate.

The geological record of sedimentary phosphate in different depositional environments is important for studies of long-term processes and interactions of the phosphorus cycle and the (paleo-)environment. In addition, in a deductive approach, the geological past may serve as a test ground for environmental inferences derived from present-day observations. This is achieved by the observation and numerical modeling of natural fluctuations and coeval changes in paleoclimate and -environments (e.g., Lerman et al., 1975; Kump, 1988; Shaffer, 1989; Compton et al., 1993; Filippelli and Delaney, 1994; Van Cappellen and Ingall, 1994).

The importance of phosphorus in the geological past is judged in different ways. For instance, in recent publications, a general decoupling of the phosphorus and carbon cycles has been emphasized for major geological periods (e.g., during the Cretaceous; Arthur and Jenkyns, 1981; during the Neogene; Delaney and Filippelli, 1994). This appears to be in contrast to the present-day observed coupling of the two elements. Related to this, it remains also unclear to what extent periods of major, widespread, phosphogenesis may be interpreted as times of globally enhanced phosphate mobilization and burial rates ("accelerated phosphorus cycle"). A further less well understood aspect in the phosphorus cycle of the present and the past are the physical and biogeochemical conditions under which phosphate is mobilized and buried in sediments (e.g., Bentor, 1980; Burnett and Froelich, 1988). Thus far, the poor understanding of these and other aspects in the phosphorus cycle and phosphogenesis have impeded a proper evaluation of the role of phosphorus in the biosphere of the present and the past. The purpose of this contribution is, therefore, to highlight these topics and relate them to the environmental significance of phosphorus.

2. The phosphorus cycle

2.1. Phosphate sources

Hydrothermal activity and submarine weathering of basalts at mid-ocean spreading centers provide negligible amounts of primordial phosphate (Baturin, 1982). According to Froelich et al. (1977, Froelich et al. (1982) and Feely et al. (1990), these processes may supply additional sinks for marine dissolved phosphate rather than constitute a globally important source, mainly because of scavenging dissolved phosphate onto suspended iron oxyhydroxides derived from hydrothermal activity, and direct uptake of phosphate through reaction with basalt (compare also Berner, 1973). Wheat et al. (1994) estimated that approximately 25–30% of the pre-industrial river flux of phosphate into the marine environment is removed by hydrothermal activity.

The contribution of continental volcanism — especially in association with the formation of apatite-bearing carbonatites (with 1–2%, locally up to 20–30% P_2O_5; Notholt et al., 1989) to the exogenic phosphorus cycle is poorly quantified, but may be important on a local to regional scale. Unknown is the significance of widespread volcanism and flood-basalt formation during episodes of plate-boundary reorganization (e.g., Schlanger et al., 1981; Rampino and Stothers, 1988; Duncan, 1991; Larson, 1991; Larson and Olson, 1991; Anderson, 1994) as a temporal supplier to the exogenic phosphorus cycle. In spite of these uncertainties, volcanic activity may represent a negligible source of phosphate when integrated over geological time.

Continental weathering of phosphate-bearing igneous and sedimentary rocks is the most important, pre-anthropogenic, source of phosphate (Fig. 1). Soils in weathering profiles constitute temporary reservoirs of phosphate, in which weathered phosphate is made bioavailable and organic phosphate is stored and transformed. Phosphate contents in soils are usually significant (0.02–1%; e.g., Sommers and Nelson, 1972; Dixon and Weed, 1989; Frossard et al., 1989; Tardy and Roquin, 1992). Phosphate behavior in soils is very much dependent on the type and quality of soil, chem-

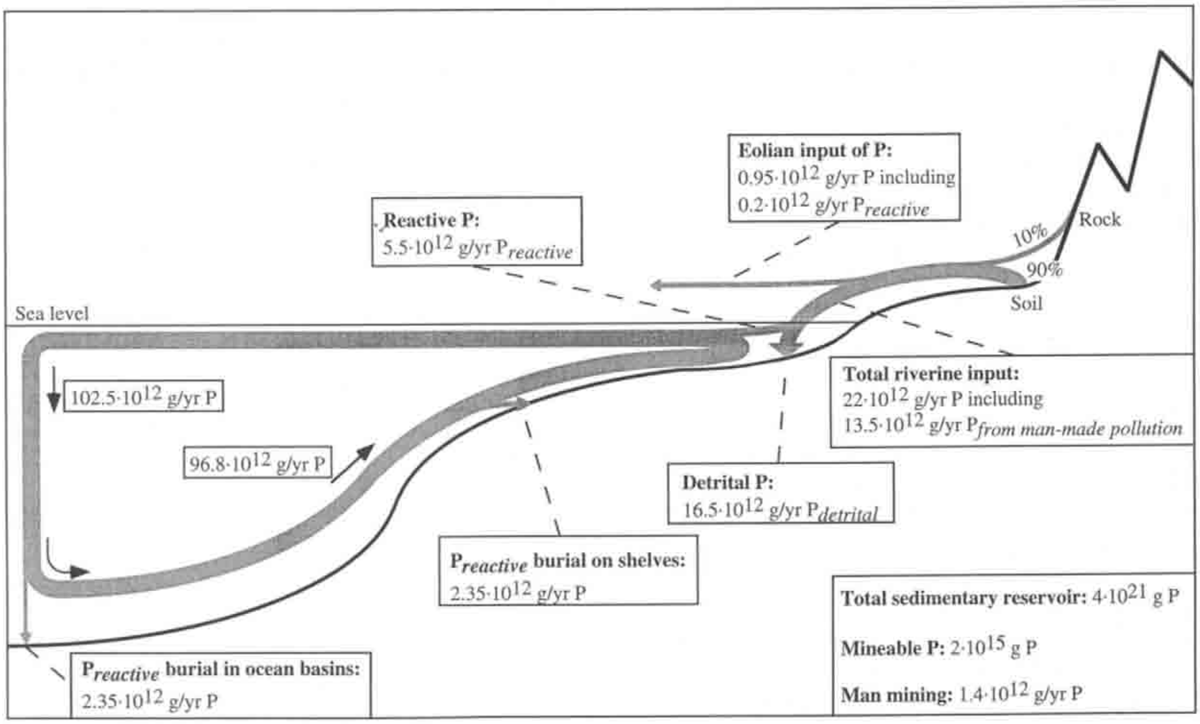


Fig. 1. Simplified diagram of the exogenic portion of the present-day global phosphorus cycle. Values are best estimates with a rather low level of confidence. Most dates were taken from Froelich (1984). Compare also Arthur and Jenkyns (1981), Moody et al. (1981, Moody et al. (1988), Baturin (1982, Baturin (1988, Meybeck (1982, Meybeck (1993), Sheldon (1982), Cook (1984), Mach et al. (1987), Froelich (1988), Duce et al. (1991), Mackenzie et al. (1993). Modified after Föllmi et al. (1993).

istry of percolating ground water, temperature, pH, degree of oxygenation and microbial activity (e.g., Smeck, 1973, Smeck, 1985; Walker and Syers, 1976; Zanin, 1989). For instance, higher temperatures, low pH and the presence of sulfate appear to promote the mobilization of phosphate, whereas the presence of Ca-rich groundwater tends to immobilize phosphate (e.g., Retallack, 1990; Koerselman et al., 1993). As an example, Adams and Walker (1975) have shown that strongly weathered and leached soils on top of granites in New Zealand lost 80% of total phosphate originally present.

2.2. *Phosphate transport pathways*

Once removed from rocks through mechanical and (bio-)chemical weathering and released from soils through leaching, phosphate is transported by water and air, and eventually transferred into lakes and oceans (Fig. 1). In rivers, approximately 95% of phosphate-containing compounds are particulate, of which 40% are organic. Dissolved organic and inorganic phosphate phases appear usually in low quantities (around 10–25 $\mu g/l$; Meybeck, 1982, Meybeck, 1988, Meybeck, 1993). A significant carrier of solid inorganic phosphate is iron oxyhydroxide, which mostly occurs in the form of aggregated colloidal suspensions or coating surfaces around suspended clay particles (e.g., Froelich, 1988; Fox, 1990). Transformations from particulate into dissolved phosphate phases and vice versa are frequently observed during river transport, due to redox changes and oxidation processes during temporary burial in river sediments and consequent reworking — especially in the case of ferric phosphate adsorbed onto redox-sensitive iron oxyhydroxides (e.g., Rao and Berner, 1993).

A non-negligible fraction of phosphate is transported through the air (approximately 4–5% of total phosphate mobilized on continents; Fig. 1; e.g., Graham and Duce, 1979; Cole et al., 1990; Duce et al., 1991; Mackenzie et al., 1993). Eolian phosphate occurs as part of mineralic dust particles, insect remains, pollen and spores, and leaf fragments. Upon deposition in marine environments, approximately 15 to 50% of total eolian phosphate is, or is made, bioavailable (Bentor, 1980; Duce et al., 1991). In terrestrial environments, the bioavailable fraction from eolian output may be enhanced considerably, because of weathering and leaching processes in soils. Eolian phosphate fluxes are of great importance to ecosystems. It is established, for instance, that a considerable portion of bioavailable phosphate in the tropical Amazon forest is derived from Saharan eolian input (estimates range between 1 and 27 kg/ha/yr phosphate; Reichholf, 1986; Swap et al., 1992).

2.3. *Phosphate sinks*

Lacustrine environments are important continental phosphate sinks. Good examples are the deposits of the Eocene Green River Formation (Wyoming and Utah; e.g., Love, 1964), the fossiliferous Eocene deposits of Messel (Germany; e.g., Schaal and Ziegler, 1992), the Pliocene Glenns Ferry Formation of Idaho (Swirydczuk et al., 1981), and the Pleistocene to recent occurrences in Lake Baikal (Deike et al., 1994). Mechanisms of phosphate enrichment and deposition have been studied in detail in different lacustrine environments (e.g., Syers et al., 1973; Carignan and Flett, 1981; Baccini, 1985; Gächter et al., 1988; Gächter and Meyer, 1993; Lazzaretti and Hanselmann, 1992) and will not be considered here. Generally, from the long-term geological perspective, lacustrine phosphate sinks may constitute rather short-lived, temporary reservoirs, which are prone to be reworked after fill-up and closure of the lake.

According to Meybeck (1982) and Froelich (1984), upon transfer from the continental environment into the marine realm, approximately 90% of total phosphate becomes buried without any interference with the marine part of the biosphere. This number may be too high, since in estuaries and river deltas significant amounts of phosphate may be transferred from the detrital to the reactive fraction of the total phosphate output, mostly in association with redox-sensitive and salinity-driven phosphate desorption reactions in iron oxyhydroxides (either as colloidal suspensions or as surface films on clay and car-

Table 1
Relative importance of inorganic and organic phosphorus sinks according to different authors. Note that the indication of P in $CaCO_3$ includes P that is adsorbed onto iron oxyhydroxide coatings on $CaCO_3$ particles and skeletons (compare Sherwood et al., 1987).

P sinks		Froelich et al. 1982	Mach et al. 1987	Berner et al. 1993	Ruttenberg 1993
Organic P	Organic matter	40%	40%	27-48%	22%
	Fish debris	<2%		22-49%	49%
Inorganic P	Authigenic PO_4	<10%	40%		
	$CaCO_3$	40%	No indication		22%
	Iron, manganese	11%	20%	0-49%	
	Loose sorption	No indication	No indication		7%

bonate particles; Froelich, 1988; Fox, 1990). Froelich (1988) estimated that, due to desorption, approximately 25% of total phosphate eroded from the contents enters the ocean in a bioavailable form.

In the marine environment, almost all reactive and bioavailable phosphate from river and eolian sources is used in the surface zone of primary productivity and incorporated into organic matter. Eventually, phosphate is transferred to the deep ocean in the form of partly aggregated organic matter and — upon oxidation — of dissolved inorganic phosphate. Most phosphate is taken up by intermediate and deep water currents and reintroduced to the photic zone by upwelling processes, where it is re-utilized by marine ecosystems (approximately 95%; Fig. 1). A small fraction (approximately 5%; Fig. 1) is removed from the ocean by sediment burial, either as organic phosphate (in organic matter and fish debris) or as inorganic phosphate through adsorption on iron and manganese oxyhydroxides or incorporation into authigenic phosphate-bearing minerals (Table 1; e.g., Berner et al., 1993). The average residence time of oceanic phosphate has recently been estimated as 16–38 kyr (Ruttenberg, 1993).

Buried inorganic phosphate in authigenic and detrital phases is mostly refractory, whereas buried inorganic phosphate adsorbed onto iron and manganese oxyhydroxides may show postdepositional mobility due to the sensitivity of these compounds to changes in redox potential (e.g., O'Brien et al., 1990; Lucotte et al., 1994). Buried organic phosphate is in many cases labile and prone to remobilization. This is in accordance with the observation that buried organic matter tends to become depleted in phosphorus relative to carbon (Froelich et al., 1982; Ingall and Van Cappellen, 1990; Berner et al., 1993). Froelich et al. (1982) calculated an average molar C/P ratio in sedimentary organic matter of 250. After burial, fish hard parts may become depleted in phosphate as well (Suess, 1981; Nriagu, 1983).

The degree and depth of diagenetic phosphate mobilization is revealed by phosphate profiles from interstitial waters. For instance, interstitial water profiles from selected Deep Sea Drilling Program (DSDP) and Ocean Drilling Project (ODP) sites show mobilization depths of phosphate up to 200–300 m below sea floor (e.g., Föllmi and Von Breymann, 1992; note, however, that interstitial phosphate data from DSDP and ODP were not collected under inert atmospheric conditions and that phosphate concentrations could be low due to coprecipitation with iron; I. Jarvis, pers. commun., 1995). Theoretically, mobilization of phosphate may be possible to the maximum depth of microbial organic-matter breakdown, which — in selected Pacific ODP sites — is over 500 m below sea floor (Parkes et al., 1994), and beyond this depth by temperature and pressure-related breakdown of organic matter.

With the development of sophisticated sequential extraction methods (e.g., Lucotte and d'Anglejan, 1985; Ruttenberg, 1992, Ruttenberg, 1993; Berner et al., 1993; Lucotte et al., 1994), it has become possible to distinguish between different buried phosphate phases preserved in sediments (e.g., Table 1). The sequential extraction method is a selective leaching procedure, which separates solid phosphate phases on the base of chemical reactivity. A distinction is made between loosely-sorbed phosphate, ferric iron bound phosphate, authigenic + biogenic + calcium carbonate bound phosphate, detrital apatite, and organic phosphate (e.g., Berner et al., 1993). An advantage of this method is the possibility to identify and quantify phosphate phases which are not detectable by standard optical and X-ray diffraction methods. For instance, discoveries of finely dispersed solid authigenic phosphate phases in marine sediments outside upwelling areas resulted from the use of sequential extraction methods (e.g., Ruttenberg and Berner, 1993; Lucotte et al., 1994; Filippelli and Delaney, in press; compare also Kim et al., 1994).

3. Formation of authigenic phosphate (phosphogenesis)

3.1. Phosphate chemistry

Phosphorites are sediments which include significant portions of authigenic and biogenic phosphate minerals. Most commonly, a lower threshold of 18% P_2O_5 is used for their definition (e.g., Jarvis et al., 1994). This threshold is somewhat arbitrary and does not take into account the usual inhomogeneous distribution of phosphate minerals in their host rock (on a mm to meter scale).

Francolite is considered to be the most common phosphate mineral that forms in early diagenetic marine environments (e.g., McClellan, 1980; Kolodny, 1981; Nathan, 1984; McClellan and Van Kauwenbergh, 1990). Its chemical composition is quite complex and variable, due to the large number of sites in which (partly coupled) substitution is possible. A valid approximation is the formula (Jarvis et al., 1994):

$$\mathrm{Ca}_{10-a-b}\mathrm{Na}_a\mathrm{Mg}_b(\mathrm{PO}_4)_{6-x}(\mathrm{CO}_3)_{x-y-z} \times (\mathrm{CO}_3\cdot\mathrm{F})_y(\mathrm{SO}_4)_z\mathrm{F}_2 \qquad (1)$$

The chemical composition of francolite is influenced by a number of variables, such as the chemical composition of sea and interstitial waters, thermodynamics and kinetics of precipitation, modes of precipitation (e.g., directly from solution or replacement of pre-existing minerals through dissolution/precipitation processes), and postdepositional alteration (e.g., during late diagenesis or weathering).

3.2. Phosphate sources and concentration mechanisms

Information on the sites and mechanisms of phosphate concentration can be obtained along

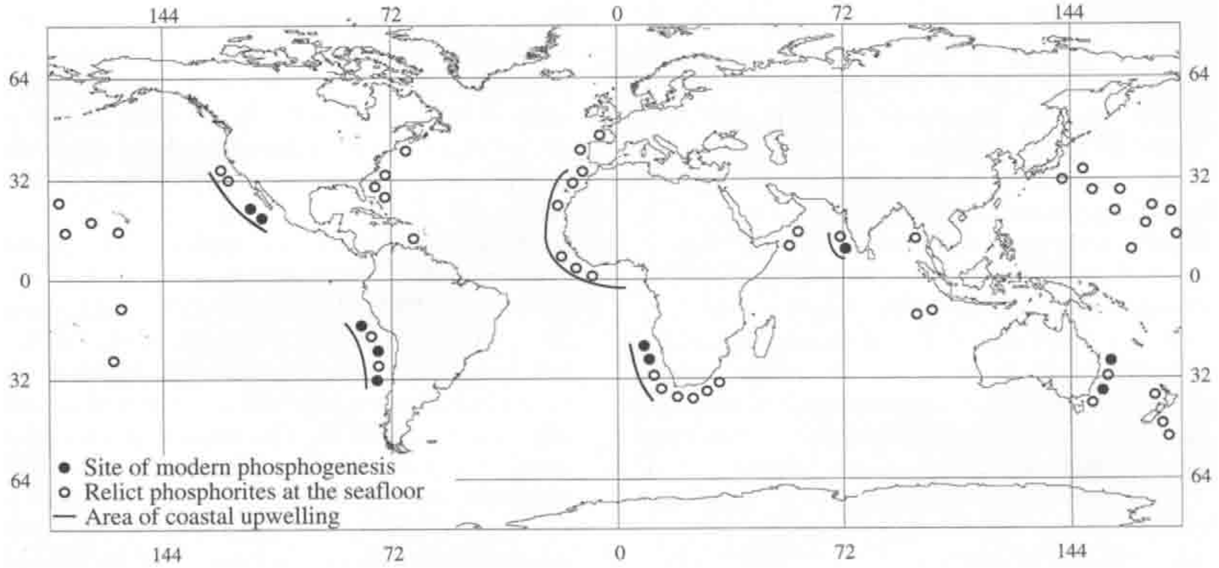


Fig. 2. World map showing sites of present-day phosphorite formation, relic phosphorites at the sea floor, and zones of coastal upwelling (modified after Baturin, 1982).

various lines. Important are geochemical and sedimentological studies in offshore sites of present-day phosphate precipitation and phosphorite formation (Fig. 2), such as the Peru–Chile margin (Veeh et al., 1973; Manheim et al., 1975; Burnett, 1977, Burnett, 1980; Burnett et al., 1980, Burnett et al., 1982, Burnett et al., 1983; Suess, 1981; Froelich et al., 1983, Froelich et al., 1988; Baker and Burnett, 1988; Burnett and Froelich, 1988; Garrison and Kastner, 1990; Glenn and Arthur, 1988; Glenn, 1990a; Glenn et al., 1994a), the western Mexico margin (D'Anglejan, 1967; Jahnke et al., 1983; Schuffert, 1988, Schuffert, 1992), the Namibian shelf (Baturin, 1971a, Baturin, 1971b, Baturin, 1982; Baturin et al., 1972; Parker and Siesser, 1972; Veeh et al., 1974; Parker, 1975; Price and Calvert, 1978; Siesser, 1978; Birch, 1979, Birch, 1980, Birch, 1990; Fuller, 1979; Birch et al., 1983; Thomson et al., 1984; McArthur et al., 1988; Bremner and Rogers, 1990; Rogers and Bremner, 1991), and the eastern Australia margin (Von der Borch, 1970; Kress and Veeh, 1980; O'Brien and Veeh, 1980, O'Brien and Veeh, 1983; O'Brien et al., 1981, O'Brien et al., 1986, O'Brien et al., 1990; O'Brien and Heggie, 1988; Riggs et al., 1989). Increasingly important are also reports on dispersed authigenic phosphate formation in marine areas outside major upwelling zones, such as nearshore and deltaic environments (e.g., Baturin, 1988; Ruttenberg and Berner, 1993; Lucotte et al., 1994). Additional information on phosphogenesis is obtained from ancient deposits (now mostly onshore), e.g., through the analysis of microstructures (e.g., Krajewski, 1984; Soudry, 1987; Lamboy, 1993), reconstruction of sedimentary environments (e.g., Jarvis, 1980, Jarvis, 1992; Southgate, 1986; Föllmi, 1989, Föllmi, 1990; Glenn, 1990b; Glenn and Arthur, 1990; Glenn et al., 1994b; Kolodny and Garrison, 1994), and geochemical inferences (e.g., Prévôt, 1990; Piper, 1994). Stable isotopes in francolite are a rich source of additional information on diagenetic conditions during phosphogenesis (e.g., McArthur et al., 1980, McArthur et al., 1986; Glenn et al.,

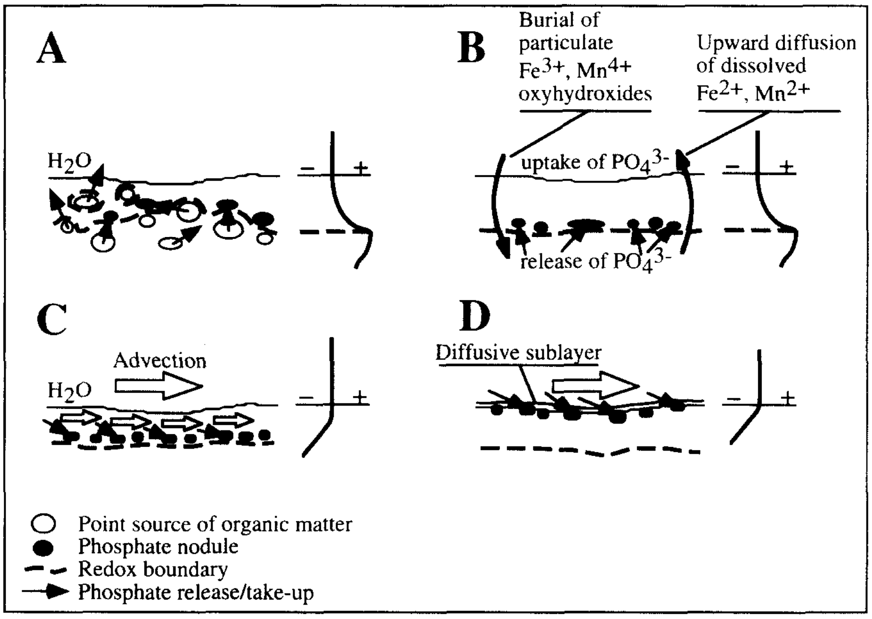


Fig. 3. Sources of dissolved phosphate and related typical phosphate pore-water curves. (A) In-vivo and post-mortem release of organic phosphate. (B) Release of inorganic phosphate through redox cycling of iron and manganese oxyhydroxides. (C) Transfer of dissolved bottom-water phosphate through subsurface flow (eddy-diffusion; diffusive sublayer not intact). (D) Transfer of dissolved bottom-water phosphate through advection/diffusion (intact diffusive sublayer). (A) and (B) Predominantly internal sources of dissolved phosphate. (C) and (D) Predominantly external sources of dissolved phosphate.

1988; Glenn, 1990a; Kastner et al., 1990; Kolodny and Luz, 1992; Jarvis et al., 1994; Kolodny and Garrison, 1994). Last but not least, models based on chemical and microbiological data from experimental phosphate precipitation have proved to be very useful in advancing our understanding of phosphate enrichment and phosphogenesis (Lucas and Prévôt, 1981, Lucas and Prévôt, 1984, Lucas and Prévôt, 1985; Jahnke, 1984; Van Cappellen and Berner, 1988, Van Cappellen and Berner, 1991; Van Cappellen, 1991).

Phosphate enrichment in sediments is accomplished in different ways. Microbial breakdown of organic matter and release of organic phosphate to pore waters represent the most fundamental internal (i.e., within sediments) source of phosphate (Figs. 3 and 4; e.g., Ingall and Van Cappellen, 1990; Berner et al., 1993; Compton et al., 1993; Van Cappellen et al., 1993; Krajewski et al., 1994). Significant portions of interstitial phosphate released by microbial breakdown of organic matter may diffuse upwards back to the sea water, especially if anaerobic bottom waters are present (Ingall et al., 1993, Ingall et al., 1994; Colman and Holland, 1994; Ingall and Jahnke, 1994; Van Cappellen and Ingall, 1994). The return of phosphate from sediments to the water is related to redox-dependent adsorption/desorption processes of phosphate onto iron and manganese oxyhydroxide and to the increased ability of microbes to store phosphate under oxic conditions (e.g., Gächter et al., 1988). The capacity of sediments to withhold phosphate from diffusive escape appears, therefore, to be oxygen dependent. Other factors controlling phosphate return rates are the rate of sediment accumulation (e.g., Ingall and Van Cappellen, 1990; Lazzaretti and Hanselmann, 1992), physical properties of the sediment, the presence of microbial mat communities at the sediment-water interface (e.g., Aller, 1994; Krajewski et al., 1994), the absence/presence of bioturbation (e.g., Aller, 1982a, Aller, 1982b), and the thermodynamics and kinetics of phosphogenesis (e.g., Van Cappellen, 1991). Colman and Holland (1994) estimated that the global diffusive phosphate flux from continental margin

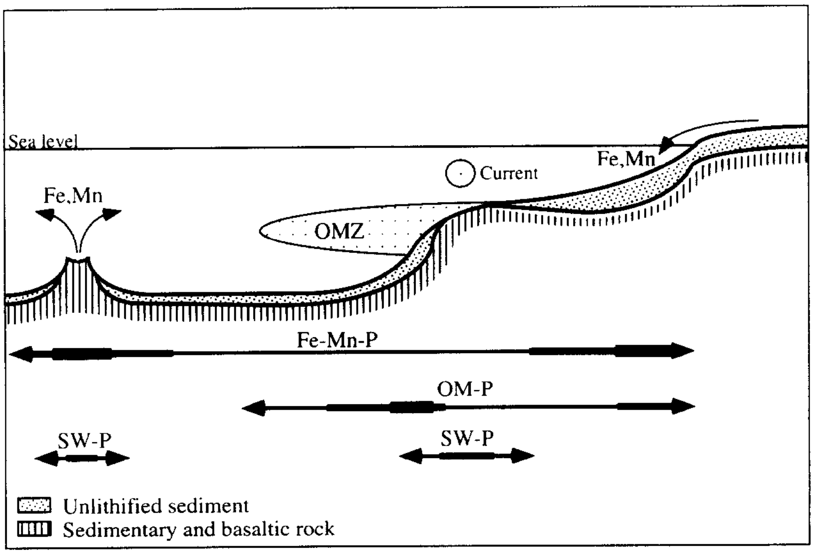


Fig. 4. Tentative overview over the relative importance of phosphate sources and concentration mechanisms in marine sediments. *Fe-Mn-P*: Interstitial phosphate release and concentration through redox-dependent phosphate adsorption/desorption processes on iron and manganese oxyhydroxides; important in nearshore environments and near sites of hydrothermal activity. *OM-P*: Interstitial phosphate release through organic matter oxidation; important in places of high primary productivity and high accumulation rates of organic matter. *SW-P*: Sea water as source of dissolved phosphate in phosphogenesis at or near the sediment-water interface; important in places of very low sediment-accumulation rates and lithified, impermeable substrates (e.g., shelf breaks, guyots).

sediments back into the oceans is an order of magnitude greater than the riverine phosphate flux to the oceans.

A second and potentially important process supplying dissolved phosphate to interstitial waters is phosphate desorption from iron and manganese oxyhydroxides upon burial or biologically induced advection (e.g., bioturbation) below the redox boundary in sediments and subsequent reduction (Berner, 1973; Froelich et al., 1977; Krom and Berner, 1980, Krom and Berner, 1981; O'Brien and Heggie, 1988; Heggie et al., 1990; O'Brien et al., 1990; Lucotte et al., 1994; compare also research on the iron cycle in lacustrine environments; Einsele, 1936; Mortimer, 1941; Stumm and Leckie, 1970; Syers et al., 1973; Baccini, 1985; Lazzaretti and Hanselmann, 1992). Generally, the susceptibility of iron oxyhydroxide towards reduction is somewhat lower than that of manganese oxyhydroxide and this may result in the preservation of relic iron oxyhydroxide — with adsorbed phosphate — in anoxic sediments, whereas manganese oxyhydroxides are usually rapidly reduced and dissolved upon transfer in anoxic sediments (Lazzaretti and Hanselmann, 1992; Lucotte et al., 1994). The "iron pump and shuttle" (e.g., Shaffer, 1986) is probably most effective in deltaic and nearshore marine environments, where fluxes of riverine iron and manganese oxyhydroxides are significant, sediment-accumulation rates are high, and bioturbation is widespread (Figs. 3 and 4; e.g., Glenn and Arthur, 1990; Glenn, 1990b). It is also important in areas near hydrothermal and submarine volcanic activity, where dissolved sea-water phosphate is scavenged by primordial iron and manganese oxyhydroxides (Berner, 1973; Froelich et al., 1977; Feely et al., 1990).

A third and less well explored source of dissolved phosphate is sea-water phosphate that directly is precipitated at the sediment–water interface (presumably with microbial assistance), or is transferred into the sediments by diffusion, or — more efficiently — by advection or eddy diffusion (e.g., Föllmi and Garrison, 1991). This process may be important at sites of phosphogenesis, in which the upward diffusion and concentration of interstitial phosphate is hindered by the presence of early diagenetically formed barriers of low permeability and in which sediment accumulation rates are negligible (allowing enough time for downward diffusion of phosphate to initiate and sustain phosphogenesis). Examples are the formation of phosphatic crusts and hardgrounds on top of lithified shallow-water and pelagic carbonates or on top of a sediment compartmentalized by stacks of earlier formed phosphate layers (Figs. 3 and 4; e.g., Schuffert, 1992).

Concentrations of dissolved phosphate in sedimentary successions are monitored by chemical analysis of stratigraphic interstitial water profiles (e.g., Froelich et al., 1983, Froelich et al., 1988; Jahnke et al., 1983; Heggie et al., 1990). In organic-rich sediments, the highest concentrations of dissolved phosphate typically occur in the uppermost part of the sedimentary column, near the sediment–water interface (however, compare also Föllmi and Von Breymann, 1992). This is related to the observation that organic matter breakdown occurs most intensely just below the sea floor, in freshly deposited sediments (e.g., Aller, 1994; Canfield, 1994; Krajewski et al., 1994), and may additionally be related to the release of iron- and manganese-bound phosphate upon reduction (e.g., O'Brien and Heggie, 1988; Lucotte et al., 1994).

3.3. Rates of interstitial phosphate enrichment

The release rates of interstitial phosphate and the supply rates of phosphate by diffusion, respectively, may be estimated with the help of general and simplified formulas. The rate of release of interstitial phosphate released from the decomposition of buried organic matter can be approximated by:

$$\partial P_{\mathrm{rel}}/\partial t = \alpha \cdot \tau \cdot (\partial P/\partial x)_t \qquad (2)$$

where P_{rel} is the amount of phosphate released to interstitial waters, t is time, x is sediment depth, α is a rate constant for the decay of organic matter, τ is the ratio of dry bulk density to porosity $= \rho_s[(1-\phi)/\phi]$, where ρ_s is average density of solid sediment grains and ϕ is porosity (i.e., mass of dry sediment grains per unit volume of pore water). $(\partial P/\partial x)_t$ is an expression of the quantity of phosphate present in the sediment in dependency of sediment accumulation rates (in volume percentage). In Eq. (2), the effect of bioturbation and physical mixing of sediments by other processes is neglected, and zero compaction and uniform porosity gradients are assumed (Berner, 1980; Van Cappellen and Berner, 1988).

∂P in Eq. (2) is dependent on the type of organic matter in a way that can be described by the following equation:

$$C_{\mathrm{org}}/P = \sigma \qquad (3)$$

where C_{org} is the amount of buried organic carbon per sediment unit in percentage. σ is a weight ratio and depends on the type of organic matter buried. For example, microbial colonies are enriched in phosphate relatively to carbon, and σ can be as low as approximately 26 (Reimers et al., 1990; Berner et al., 1993); for buried planktic organic matter, the Redfield ratio can be assumed (mole ratio = 106) and σ is approximately 40 (compare Redfield et al., 1963; Takahashi et al., 1985). Note that the above does not take into account the observation that, during early diagenesis, phosphate is released at increased rates relative to carbon from decomposing organic matter and that, in general, the C/P molar ratio is 250 in preserved organic matter (Froelich et al., 1982).

If Eq. (3) is substituted in Eq. (2), we obtain:

$$\partial P_{\mathrm{rel}}/\partial t = \alpha \cdot \tau \cdot \left(\partial\left[C_{\mathrm{org}}/\sigma\right]/\partial x\right)_t \qquad (4)$$

Phosphate released to interstitial waters may either be precipitated as francolite, absorbed onto iron and manganese oxyhydroxides, or removed by diffusion processes across the sediment/water interface. In the case of francolite precipitation, we may substitute (after Ouwehand, 1987):

$$\partial A/\partial t = \left[\partial P_{\mathrm{rel}}/\partial t - \left(\partial P_{\mathrm{abs}} + \partial P_{\mathrm{diff}}\right)/\partial t\right] \cdot (5.3/2.9) \qquad (5)$$

where A is the thickness of the formed solid francolite layer, $P_{\mathrm{abs}} + P_{\mathrm{diff}}$ is the amount of absorbed and diffused phosphate not available for incorporation into solid francolite, 5.3 is a constant to convert phosphate into francolite, based on the molecular/weight ratio of 504/95 and on the simplified formula $Ca_5(PO_4)_3F$ (i.e., fluorapatite; Ouwehand, 1987), and 2.9 (g/cm^3) is the specific weight of francolite. Substituting Eq. (4) into Eq. (5), we obtain:

$$\partial A/\partial t = \left\{\alpha \cdot \tau \cdot \left(\partial\left[C_{\mathrm{org}}/\sigma\right]/\partial x\right)_t - \left(\partial P_{\mathrm{abs}} + \partial P_{\mathrm{diff}}\right)/\partial t\right\} \cdot (5.3/2.9) \qquad (6)$$

An estimate for the importance of phosphate release from organic matter decay can be obtained if a highly simplified scenario is assumed in which all conditions are highly favorable to phosphogenesis. In the following example, a finite sediment layer is deposited instantaneously (as a turbidite or tempestite layer, for instance) and background sediment-accumulation rates are suppressed (i.e., $\partial(C_{\mathrm{org}}/\sigma)/\partial x) = d \cdot \partial(C_{\mathrm{orgtot}}/\sigma)/\partial t$, where C_{orgtot} equals the total amount of organic matter present in the layer under consideration and d is the thickness of the layer). All phosphate incorporated into organic matter is released and subsequently precipitated in the form of francolite (i.e., $\alpha = 1$; $\partial P_{\mathrm{abs}} + \partial P_{\mathrm{diff}}/\partial t = 0$). If we also assume that for general cases ϕ is 80% and ρ_s is 2.5 g/cm^3 (i.e., $\tau = 0.625$), then:

$$A_{\mathrm{tot}} = 0.625 \cdot d \cdot \left(C_{\mathrm{orgtot}}/\sigma\right) \cdot (5.3/2.9) \qquad (7)$$

Given the case of a 10 cm thick bed, in which 25 wt.% planktic organic matter with $\sigma = 40$ is trapped:

$$A_{\mathrm{tot}} = 0.625 \cdot 10 \cdot (0.25/40) \cdot (5.3/2.9) = 0.071\,\mathrm{cm\ francolite} \qquad (8)$$

This theoretical scenario is in extreme favor of francolite precipitation. Commonly not all included organic matter will be decomposed and not all dissolved interstitial phosphate will be incorporated into solid francolite, so that in reality the above value may be lowered by an order of magnitude. Still, this example shows that organic matter decay is a potentially important source of interstitial dissolved phosphate, with general rates of phosphate release depending on the susceptibility of organic matter to decomposition (e.g., Canfield, 1993, Canfield, 1994).

The release of dissolved phosphate by redox cycling of iron and manganese oxyhydroxides can be quantified with the general formula:

$$\partial P_{\mathrm{rel}}/\partial t = \mu \cdot \tau \cdot \left[(\partial M_{\mathrm{red}}/\partial x)_t + (\partial M_{\mathrm{red}}/\partial x)_{\mathrm{biot}} \right] \tag{9}$$

where μ is a proportional factor related to the amount of phosphate bound to redox metals, and the term $(\partial M_{\mathrm{red}}/\partial x)_{\mathrm{biot}}$ the amount of redox metals brought into the sediments by sediment accumulation and bioturbation per time unit in percentage. The effect of a fluctuating redox boundary is neglected in this formula (e.g., Aller, 1994).

In order to estimate the effectiveness of iron and manganese oxyhydroxide as a source for dissolved phosphate, again an example is used in which a sediment layer with finite dimensions is assumed (sediment accumulation rates are zero):

$$\partial P_{\mathrm{rel}}/\partial t = \mu \cdot \tau \cdot d \cdot \left[(\partial M_{\mathrm{red}}/\partial t) + (\partial M_{\mathrm{red}}/\partial t)_{\mathrm{biot}} \right] \tag{10}$$

In this example, the layer has a thickness of 10 cm and includes 6 wt.% oxidized iron and manganese, from which 5% inorganic phosphate is released ($d = 10$ cm, $\mu = 0.05$, $\tau = 0.625$; e.g., Van Cappellen and Berner, 1988; Föllmi and Garrison, 1991). Bioturbation and redox cycling is neglected in this case. Assuming that all released dissolved phosphate will be converted into solid francolite, we obtain:

$$\begin{aligned} A_{\mathrm{tot}} &= \mu \cdot \tau \cdot d \cdot M_{\mathrm{tot}} \cdot (5.3/2.9) \\ &= 0.05 \cdot 0.625 \cdot 10 \cdot 0.06 \cdot (5.3/2.9) \\ &= 0.034 \, \text{cm francolite} \end{aligned} \tag{11}$$

This theoretical amount of francolite indicates that redox-metal related inorganic sources of dissolved phosphate may account for a substantial portion of phosphate enrichment in sediments.

Diffusion of dissolved phosphate across the sediment–water interface may generally be an important source of phosphate, especially after depletion or diagenetic sealing of internal phosphate sources and the formation of strong phosphate sinks below or at the sediment–water interface (i.e., phosphatized particles, lenses or laminae). The diffusive flux of dissolved phosphate across the sediment–water interface is quantified by the formula (Vanderborght et al., 1977; Suess, 1981):

$$\partial P/\partial t = d_P \cdot (\partial C_P/\partial x)_t \tag{12}$$

where d_{P} is the diffusion coefficient of dissolved phosphate in interstitia, and C_{P} is the concentration of dissolved phosphate at the sediment–water interface. Krom and Berner (1980) have calculated a value of 1.3×10^{-6} cm^2/s for the diffusion coefficient of phosphate in nearshore organic-rich muds of Long Island Sound, USA. This value is used herein.

As an illustrative example of the relative importance of phosphate diffusion, we assume a value of 2×10^{-8} mol/cm^3 = 6.25v6,3910^{-7} g/cm^3 for dissolved reactive phosphate in the bottom waters of our example — a value comparable to the modern-day upwelling area offshore Baja California (Jahnke et al., 1983; = 10 times the average value for offshore Peru and California; compare Suess, 1981: 2×10^{-9} mol/cm^3; Sholkovitz, 1973: approximately 3.5×10^{-9} mol/cm^3), and a complete transfer of interstitial phosphate into solid francolite, we obtain an increment in francolite of:

$$\begin{aligned} A_{\mathrm{tot}}/\mathrm{yr} &= 3.1536 \times 10^{7} \cdot 1.3 \times 10^{-6} \cdot 6.25 \times 10^{-7} \\ &\quad \cdot (5.3/2.9) \\ &= 4.7 \times 10^{-5} \, \text{cm/yr francolite} \end{aligned} \tag{13}$$

This value indicates that thousands of years are needed to construct a macroscopic francolite layer using pure diffusion across the sediment–water interface as the unique phosphate source. This value changes positively, when we take into consideration an advection/diffusion-induced transfer of phosphate, driven by the movement of waters along the sea floor. We can distinguish between two cases: (1) the shearing stress of turbulent bottom-water movement is strong enough to locally disturb the diffusive sublayer on top of the sediment–water interface and to induce a subsurface flow in the uppermost sediments (commonly coupled with erosion and winnowing); (2) turbulent bottom-water movement leaves the diffusive sublayer intact. These two cases are highly idealized end-members of a continuum in space and time; e.g., episodic turbulent "bursts" in bottom-water movement may temporarily delete the diffusive sublayer and the presence of topographic irregularities (e.g., phosphatized particles; organic structures) may cause spatial discontinuities within the diffusive sublayer (Berner, 1980; Boudreau, 1988; Gundersen and Jørgensen, 1990; Libelo et al., 1994).

In case 1, the subsurface water flow leads through eddy diffusion to a flux of dissolved phosphate into interstitia, which is higher than that predicted by pure diffusion. For example, Vanderborght et al. (1977) calculated for North-Sea sediments a convection-induced mass-transfer coefficient of dissolved silica in the uppermost 3.5 cm of the sediment surface 100 times higher than that for pure diffusion. Correspondingly, if a similar increase is assumed for phosphate, time spans of phosphate formation would be shortened by two orders of magnitude in comparison to pure diffusion (4.7×10^{-3} in comparison to 4.7×10^{-5} cm/yr in the above example).

In case 2, assuming an undisturbed diffusive sublayer, the turbulent movement of water will result (along paths that are difficult to quantify) in a net increase in the concentration of dissolved phosphate in the diffusive sublayer (Morse, 1974; Boudreau and Guinasso, 1982; Boudreau, 1988; Segl et al., 1989; Santschi et al., 1990; Atkinson and Bilger, 1992; Bilger and Atkinson, 1992). This concentration gradient is a function of the thickness of the diffusive boundary layer, the velocity of bottom waters, bottom-water phosphate concentrations and the presence of strong phosphate sinks at or below the sea floor, and can be expressed by the simplified formula (e.g., Boudreau and Guinasso, 1982; Segl et al., 1989; Gundersen and Jørgensen, 1990):

$$\partial P/\partial t = \beta \cdot \partial(C_P - C_o)/\partial t \qquad (14)$$

where β is the mass-transfer coefficient (proportional to water velocity, kinematic viscosity, and the diffusion coefficient of phosphate in water; Boudreau and Guinasso, 1982; Segl et al., 1989); C_P is the concentration of dissolved phosphate above the sediment–water interface, and C_o is the concentration of dissolved phosphate within the diffusive sublayer. Segl et al. (1989) empirically estimated a twofold increase in the flux of manganese and iron corresponding to a two to threefold increase in bottom-water velocity. They suggested that concentrations within the diffusive sublayer can rise to values up to 40 times the original value within the water column with rising bottom water velocities (maximum bottom-water velocities around 20 cm/s). Transposed to our example, this would lead to a significant increase in phosphate formation in comparison to pure diffusion.

The above cursory calculations using theoretical examples suggest that the delivery and interstitial enrichment of organically bound phosphate from within sediments and the supply of inorganically bound phosphate via iron and manganese redox cycles is measurable in time spans of years to kiloyears, and substantial amounts of phosphate can be transferred in these ways, if conditions are favorable. The delivery of phosphate through diffusion or advection/eddy diffusion across the sediment–water interface is measurable in time spans of kiloyears and more, and the amount of dissolved phosphate transferred per time unit may be lower on the order of one or two magnitudes in comparison to the aforementioned sources.

3.4. Sedimentology and phosphate enrichment in areas of present-day phosphorite formation

Marine areas of present-day phosphogenesis and phosphorite formation show a set of sedimentological conditions that is typical and common to all, and decisively influences patterns and rates of phosphate enrichment and phosphorite formation.

Net sediment-accumulation rates in the Pacific area offshore Baja California are low to virtually zero (Fig. 2; Jahnke et al., 1983; Schuffert, 1988). D'Anglejan (1967) reported phosphatic particles from an extensive erosional platform, on which Pliocene and Pleistocene sediments are partly reworked into a phosphate-bearing sand cover of variable thickness on top of partly exposed Miocene sediments. D'Anglejan (1967) attributed sedimentary reworking processes to erosional and redepositional phases related to sea-level changes, but also reported the presence of longshore current activity (southbound California Current overriding the northbound North Equatorial Current).

In the Pacific offshore Peru and Chile, phosphorites have been observed in sediments of middle Miocene to Holocene age, all exposed at the sea floor. The phosphorites consist of soft and friable phosphatic nodules, indurated phosphatic particles, and complex crusts (Veeh et al., 1973; Manheim et al., 1975; Burnett, 1977, Burnett, 1980; Burnett et al., 1980; Baker and Burnett, 1988; Froelich et al., 1988; Glenn and Arthur, 1988; Garrison and Kastner, 1990; Glenn et al., 1994a). Sediment-reworking processes such as erosion, winnowing and slumping play a prominent role in this area, and the indurated nodules and complex crusts bear witness of the effect of persistent high-energy levels (Burnett, 1977; Garrison and Kastner, 1990; Glenn et al., 1994a). Bottom-hugging current systems are held responsible for the sediment-reworking processes and the resulting large variations in sediment-accumulation rates, as well as the presence of multiple sedimentary unconformities including hiatuses of variable time spans (DeVries and Schrader, 1981; Burnett et al., 1983; Reimers and Suess, 1983).

Phosphatic laminae, particles and lithoclasts of middle Eocene to modern age have been dredged from various sites offshore Namibia and South Africa (Baturin, 1971a, Baturin, 1982; Veeh et al., 1974; Price and Calvert, 1978; Birch, 1979, Birch, 1980; Birch et al., 1983; McArthur et al., 1988; Bremner and Rogers, 1990; Rogers and Bremner, 1991). Extensive sedimentary reworking appears to have been the principal agent of sediment distribution processes within the entire documented time span. Currently, the Benguela Current is shown to be responsible for sediment reworking (Calvert and Price, 1970; Baturin, 1971b).

In the Pacific offshore East Australia, on the shelf and adjacent slope offshore New South Wales, condensed phosphatic hardgrounds, both friable as well as indurated phosphatic particles, and phosphatized fossils ranging in age from Miocene to modern are known. The environments of phosphate deposition are generally described as areas of extensive sediment reworking promoted by the bottom-scouring East Australian Current (Von der Borch, 1970; Kress and Veeh, 1980; O'Brien and Veeh, 1980; O'Brien et al., 1981; O'Brien and Heggie, 1988; Riggs et al., 1989).

Offshore environments with reported accumulations of fossil phosphatized particles and nodules on the sea floor, yet lacking evidence for recent phosphogenesis, are very similar to the above environments; i.e., they are consistently current-influenced, exhibit characteristic low, zero, or even negative sediment-accumulation rates, and are or have been sites of extensive sediment reworking (e.g., offshore California: Lower to Middle Miocene phosphates; Dietz et al., 1942; Mullins and Rasch, 1985; Blake and other plateaus offshore Florida and South Carolina: Miocene phosphates; Manheim et al., 1980; Riggs, 1984; Agulhas Plateau offshore South Africa: Middle Miocene to Pliocene phosphates; Murray and Renard, 1891; Collet, 1906; Parker and Siesser, 1972; Parker, 1975; Siesser, 1978; Fuller, 1979; Flemming, 1981; Martin et al., 1982; Tucholke and Embley, 1984; Chatham Rise offshore East New Zealand: Miocene phosphates; Von Rad and Rösch, 1984; Von Rad and Kudrass, 1987; amongst other areas; compare overview in Kolodny, 1981).

All these areas are characterized by current-dominated sedimentary regimes with correspondingly low net sediment-accumulation rates. Current dynamics are responsible for an interplay between sediment aggradation, reworking and dislocation, an interplay which has first been described by Baturin (1971a) as typical for areas of phosphorite formation and was subsequently designated by the term "Baturin" cycles (Mullins and Rasch, 1985). Moreover, the areas of significant present-day phosphorite formation are associated with high primary productivity rates in the surface waters due to coastal, partly obstructional upwelling of phosphate-enriched waters (Fig. 2). An apparent exception is the eastern Australian phosphorite province which is exposed to seasonal upwelling resulting only in moderate rates of primary productivity. Indeed, the degree of present-day phosphorite formation is around one order of magnitude lower compared to those of the offshore Peru–Chile and offshore Namibia areas (Riggs et al., 1989).

In these areas of modern phosphorite formation, phosphate-enrichment is accomplished by early diagenetic decomposition of organic matter and by iron and manganese redox cycles. Organic matter decomposition is probably more important in those areas of most intense primary productivity, characterized by the presence of pronounced oxygen-minimum zones and the development of laminated sediments, whereas iron and manganese redox cycles are more important in areas of significant detrital sediment input and bioturbation of the uppermost sediment layer (e.g., Heggie et al., 1990; O'Brien et al., 1990). In areas of most intense current activity and formation of extensive phosphate crusts and other early diagenetic barriers, advection and eddy diffusion of dissolved inorganic phosphate is thought to be important as well.

The lack of modern phosphogenesis in the areas with relic phosphorites at the sea floor (Fig. 2) could be related to the circumstance that these areas may be in or close to sedimentary equilibrium, i.e., in a steady-state situation in which major event deposition and lateral sediment dislocation is absent (e.g., Dott, 1988). This relates to a sedimentary mechanism of interstitial phosphate enrichment which is reviewed in the following chapter.

3.5. *Sudden burial, a potentially effective mechanism of interstitial phosphate enrichment*

An additional mechanism affecting interstitial phosphate enrichment may be sediment dislocation events and resulting sudden burial of benthic and benthos-related organisms (Föllmi, 1989, Föllmi, 1990; Föllmi and Garrison, 1991). This mechanism may be effective if significant amounts of pristine organic matter are rapidly buried and

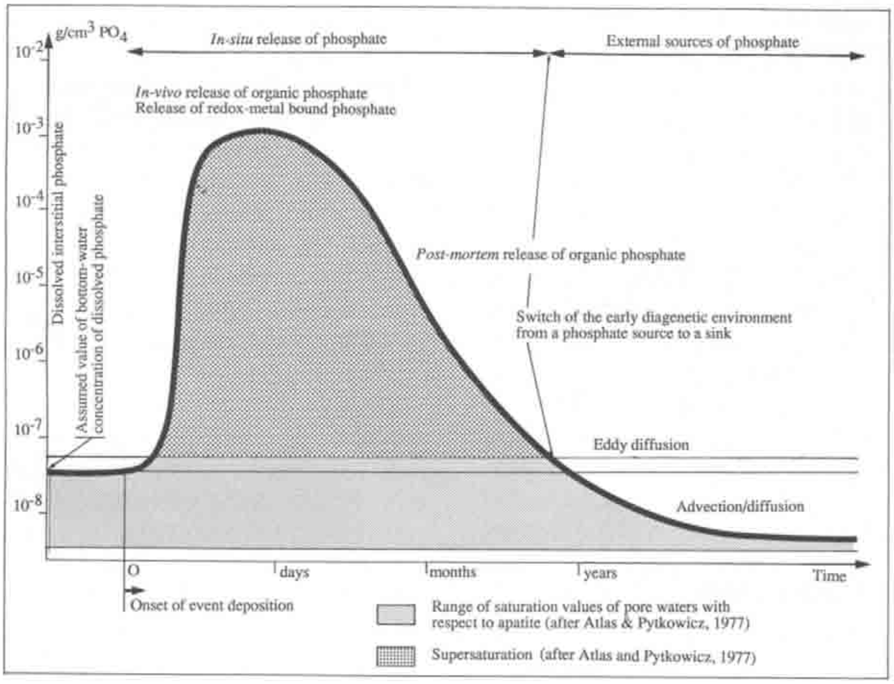


Fig. 5. Hypothetical time-interstitial dissolved phosphate concentration diagram for the case of sudden burial of large amounts of pristine microbial organic matter by event deposition in a current-dominated sedimentary regime with low net sediment-accumulation rates. Note the steep positive gradient after sudden burial, the subsequent slow decrease in concentrations of dissolved phosphate, and the switch from internal to external sources of dissolved phosphate (modified from Föllmi and Garrison, 1991).

a temporary, very reactive, early diagenetic environment is created in which phosphate enrichment may take place at rapid rates. In addition, sudden burial of microbial colonies and the rapid development of anoxia may help to build up levels of interstitial dissolved phosphate through the in-vivo release of phosphate (Gächter et al., 1988; see Section 3.7.).

In general, sudden burial of pristine organic matter may lead to the rapid development of sulfate-reducing zones within and around the organic matter (Goldhaber and Kaplan, 1975; Berner, 1977; Westrich and Berner, 1984; De Lange et al., 1987). This in turn will result in the establishment of a sharp and focused redox boundary, characterized by the near coincidence of O_2, Fe and Mn redox boundaries; Coleman, 1985; Jarvis and Higgs, 1987). Subsurface advection of oxygenated waters may also contribute to this process of focusing. In the case of an irregular distribution of buried organic matter (e.g., buried macrobenthos), anoxic microenvironments form and a complex early diagenetic environment results, in which areas of available oxygen and of sulfate reduction co-exist on an intimate scale. In such complex diagenetic systems, the available redox-boundary surface per sediment unit is considerably enhanced and the intensity of redox reactions increased (e.g., Tyson, 1987).

The mechanism of sudden burial may lead to a rapid initiation of phosphogenesis, which may proceed until internal phosphate sources are depleted. Continued phosphogenesis, however, is only possible by maintaining the phosphatized particles at or near the sediment–water interface through repeated cycles of sudden burial and consequent sediment-removal ("Baturin cycles"), with the possible addition of advection and eddy diffusion of dissolved seawater phosphate (Fig. 5).

The mechanism of sudden burial, phosphogenesis and consequent sediment removal may explain the presence of well-preserved, phosphatized, organisms in highly condensed phosphatic

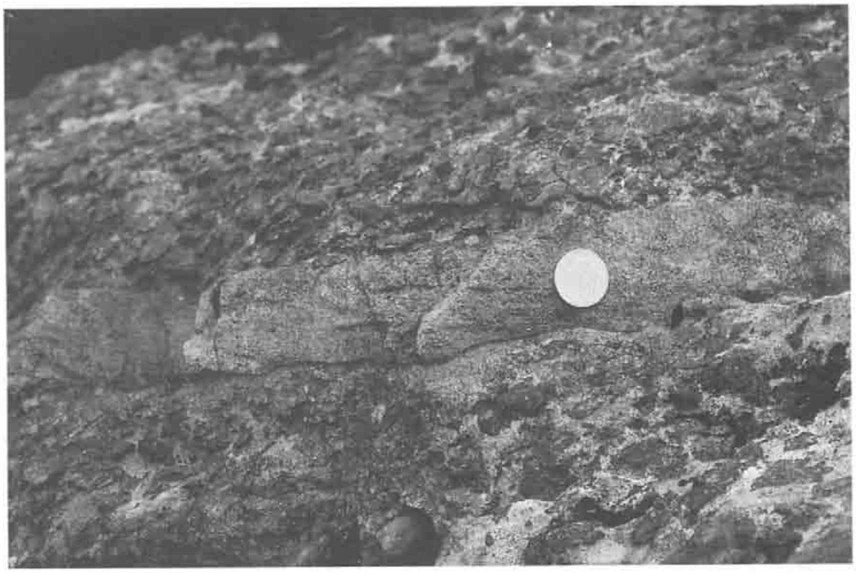


Fig. 6. Example of the possible effect of sudden burial on phosphogenesis and phosphate accumulation. The bed shown is highly condensed, approximately 1 m thick, and includes fossils which document the time interval from the Aptian–Albian boundary to the early Turonian. Fossils are abundant and well preserved (silicisponges, gastropodes, inoceramid bivalves, ammonoids, echinoids, etc.). The phosphate particles show different phosphate generations, which document the effect of multiple sediment reworking events. At this locality, the bed includes an approximately 70 cm long and 4 cm thick lense of cross-bedded, non-phosphatized, glauconitic quartz sand which represents a relic sediment transported in offshore direction (compare Fig. 14). Plattenwald Bed, Col de la Plaine Morte, central Swiss Alps (coin diameter = 2.3 cm).

beds (Föllmi, 1989, Föllmi, 1990) and may taphonomically be comparable to "obrution" deposits (rapid entombment within sediment; Seilacher et al., 1985; Brett et al., 1986; Brett, 1988; Speyer and Brett, 1988). Records of sediment-burial events in phosphate-rich deposits may be recognized if: (1) well-preserved fossils documenting episodes of rapid fossilization and phosphatization are present in otherwise condensed phosphatic beds; (2) heterogeneous mixtures and different generations of phosphates occur, documenting the effect of several or multiple phases of sediment burial, phosphogenesis, and sediment removal ("Baturin cycles"); (3) lenses of non-phosphatized relic sediments are included in otherwise phosphatic beds (Fig. 6), suggesting sediment bypassing (sediment bypassing, however, can only be positively demonstrated in onshore deposits, when facies and sediment distribution are compared on a larger, paleogeographic scale; see below).

3.6. Phosphate precipitation

The equilibrium value of pure fluorapatite [$Ca_5(PO_4)_3F$] is estimated to vary between 5×10^{-8} g/l and 2.5×10^{-7} g/l, for ranges of pH between 7.1 and 7.8, and T between 5 and 20°C (Atlas and Pytkowicz, 1977; Van Cappellen and Berner, 1988; Fig. 5). The composition of precipitated phosphate (especially the carbonate content), sediment properties, the presence of oxygen and microbial mediation may considerably change these values which were measured experimentally under conditions of thermodynamic equilibrium (Jahnke, 1984; Van Cappellen and Berner, 1988; Van Cappellen, 1991).

Sea water contains approximately 6×10^{-5} g/l dissolved phosphate on average (Turekian, 1969; Van Cappellen, 1991). Large areas of sea water are, for this reason, probably saturated with respect to francolite (e.g., Van Cappellen, 1991; Jarvis et al., 1994). However, due to the slow kinetics of francolite precipitation, francolite is probably only formed at the sediment–water interface if sediment-accumulation rates are slow enough to permit for the transfer of substantial amounts of dissolved phosphate onto the sediment–water interface and/or if preformed phosphatic particles are present at the sediment–water interface, providing reactive surface areas and acting as templates for further francolite accretion (e.g., Boudreau, 1988, who described a similar scenario for the growth of manganese nodules at the sediment–water interface). Microbial mediation is probably a further important prerequisite (compare Section 3.7.).

Pore waters show dissolved phosphate values which are typically higher than those for sea water and supersaturation with respect to francolite is probably the rule (e.g., Van Cappellen, 1991). In the case of high rates of interstitial supersaturation with respect to francolite (i.e., 10^{-2} to 2×10^{-2} g/l), francolite precipitation is experimentally determined to be a rapid (i.e. hours to days) two-step process, via an amorphous precursor {either struvite ($NH_4MgPO_4 \cdot 6H_2O$); Malone and Towe, 1970; Lucas and Prévôt, 1985; Prévôt et al., 1989; amorphous calcium phosphate (ACP); Froelich et al., 1988; or octacalcium phosphate [OCP, $Ca_4H(PO_4)_3 \cdot xH_2O$]; Van Cappellen, 1991; Van Cappellen and Berner, 1991; compare also Jarvis et al., 1994; Krajewski et al., 1994}. Once the metastable precursor phase has formed, it is used as a substrate for francolite precipitation.

In the case of lower levels of supersaturation with respect to francolite (i.e., 3×10^{-3} to 10^{-2} g/l), francolite is precipitated directly, but slowly (i.e., months to years), without intermittent precursor formation (Van Cappellen, 1991). Rapid francolite precipitation with intermittent precursor formation is suspected to take place in the Pacific areas of present-day phosphorite formation offshore Peru and Chile (Froelich et al., 1988), whereas slow francolite precipitation without intermittent precursor formation is suggested to take place in rapidly accumulating sediments outside major upwelling cells (leading to dispersed phosphogenesis; e.g., Baturin, 1988; Van Cappellen, 1991; Ruttenberg and Berner, 1993).

Francolite precipitation takes place either directly, through nucleation and crystallization on mineral surfaces, biological soft and hard parts, and biofilms, or through dissolution/precipitation replacement of existing minerals (mostly calcium carbonate; compare Prévôt and Lucas, 1986; Lamboy, 1993). Once formed, the francolite nuclei serve as a template for further francolite accretion, until interstitial dissolved phosphate levels are too low to sustain further precipitation (Van Cappellen, 1991) or until levels of alkalinity are high enough to prevent further francolite precipitation (Baturin and Savenko, 1985; Glenn et al., 1988). Initially formed francolite crystallites are not larger than 0.1–10 mm, due to growth kinetics (Van Cappellen, 1991; Van Cappellen and Berner, 1991). They are typically rod-shaped, with round terminations and subcircular cross sections (e.g., Krajewski et al., 1994). With aging, francolite attains a better crystallinity (on a time scale of 10 to 100 yr; Gulbrandsen et al., 1984; Jarvis et al., 1994).

Several chemical constituents have been identified, which may inhibit or catalyze francolite precipitation: (1) low levels of interstitial dissolved sulfate appear to favor phosphogenesis (Caraco et al., 1989); (2) the presence of Mg in interstitial water is experimentally shown to retard francolite precipitation (Nathan and Lucas, 1976; Atlas and Pytkowicz, 1977; Van Cappellen, 1991; Van Cappellen and Berner, 1991; Jarvis et al., 1994); (3) lowering interstitial pH (from 8 to 7) is also experimentally shown to favor phosphogenesis, in spite of the increased solubility of francolite (Van Cappellen, 1991); (4) relevant with regards to the process of phosphogenesis is the extent to which phosphogenesis is redox-dependent: Arthur and Jenkyns (1981), Coleman (1985), Ouwehand (1987), Heggie et al. (1990), Glenn et al. (1994b), Jarvis et al. (1994) and Van Cappellen and Ingall (1994) argued for oxic to suboxic environments. Anoxic environments have been envisaged by Baturin (1971a), Burnett (1977), Bentor (1980), Manheim et al. (1980), Kolodny (1981), Froelich et al. (1983), Jahnke et al. (1983) and Glenn and Arthur (1988). Tooms et al. (1969) and Baker and Burnett (1988) pointed to independency from redox conditions, and Jarvis (1980), McArthur et al. (1986), Meunier et al. (1987) and Krajewski et al. (1994) considered fluctuating redox potentials as important to phosphogenesis. Trace elements in sedimentary phosphates of different localities include both oxidized and reduced ions such as sulfate (Jahnke, 1984; Nathan, 1984), and U^{6+} and U^{4+} (Bentor, 1980; Burnett et al., 1980; Kolodny, 1981; Slansky, 1986). The ambiguous redox signature in phosphates is also reflected by variations in $\partial^{34}S$ and $\partial^{13}C$ (McArthur et al., 1986). However, changes in the isotopic composition may also happen during late stages of diagenesis (Leather and Kastner, 1989; Kastner et al., 1990).

The main locus of phosphogenesis in phosphorite-forming sediments appears to be situated near the sediment–water interface, in the suboxic zone close to the redox boundary (e.g., Jarvis et al., 1994). Based on stable carbon isotopes in dredged phosphorites from the Peru–Chile margin, Glenn et al. (1988) suggested a depth of phosphogenesis within a few centimeters of the sediment–water interface. They inferred that, at greater sediment depths, phosphogenesis may be impeded by rising alkalinity, due to organic matter breakdown (Jahnke, 1984; Glenn et al., 1988). Anoxia appears to promote the microbial release of dissolved phosphate (Jarvis and Higgs, 1987; Gächter et al., 1988 Ingall et al., 1993, Ingall et al., 1994; Ingall and Jahnke, 1994; Van Cappellen and Ingall, 1994) and leads to desorption of phosphate from iron and manganese oxyhydroxides (e.g., Heggie et al., 1990; Lucotte et al., 1994). In laboratory experiments, phosphate precipitation is accelerated if the solution is constantly aired (Vaillant, 1987; Hirschler, 1990).

Oxic to suboxic conditions may be a favorable prerequisite, but are certainly not a necessary condition for phosphogenesis. In spite of the aforementioned increased solubility of phosphate in anoxia and increased alkalinity in deeper parts of the sediment, phosphogenesis is still feasible in anoxic sediments, especially if preformed phosphatic particles or phosphate-bearing organic material (e.g., fish and vertebrate skeletons, coprolites) are present, which serve as a template for francolite accretion and replacement. Possible examples of phosphogenesis in fully anoxic sediments are phosphatized organisms and coprolites occurring in laminated, organic-rich sediments of the mid-Triassic "Grenzbitumenzone" (southern Alps of Switzerland and northern Italy), which are inferred to have originated below an anoxic lower water mass separated from an upper oxygenated water mass by a mid-water redox boundary (Bernasconi, 1994; Fig. 7). Phosphatized fossils and coprolites in the Eocene lacustrine organic-rich muds of Messel (Germany), interpreted to have been deposited below an anoxic water mass, provide a further example (Schaal and Ziegler, 1992). In a recent contribution, Schimmelmann et al. (1994) described the occurrence of a phosphatized coprolite (presumably of human origin) approximately 70–80 cm below the sediment–water interface in anoxic sediments of the Santa Barbara Basin.

Phosphogenesis appears also to take place in deeper parts of the sediments, under later-stage diagenetic conditions. Petrographic observations indicate that francolite, rich in structural carbonate, can undergo dissolution and replacement by francolite enriched in fluorine (J. Lucas, pers. commun., 1994). This process could also be responsible for diagenetic porosity-filling francolite cementation in, for instance, phosphate-rich turbidites in pelagic sediments or along shear zones in compaction-deformed sediments (e.g., Föllmi and Von Breymann, 1992). Stable carbon isotopes also point to the transformation of a significant fraction of francolite during later stages of diagenesis (e.g., Kolodny and Garrison, 1994).

3.7. Microbial involvement

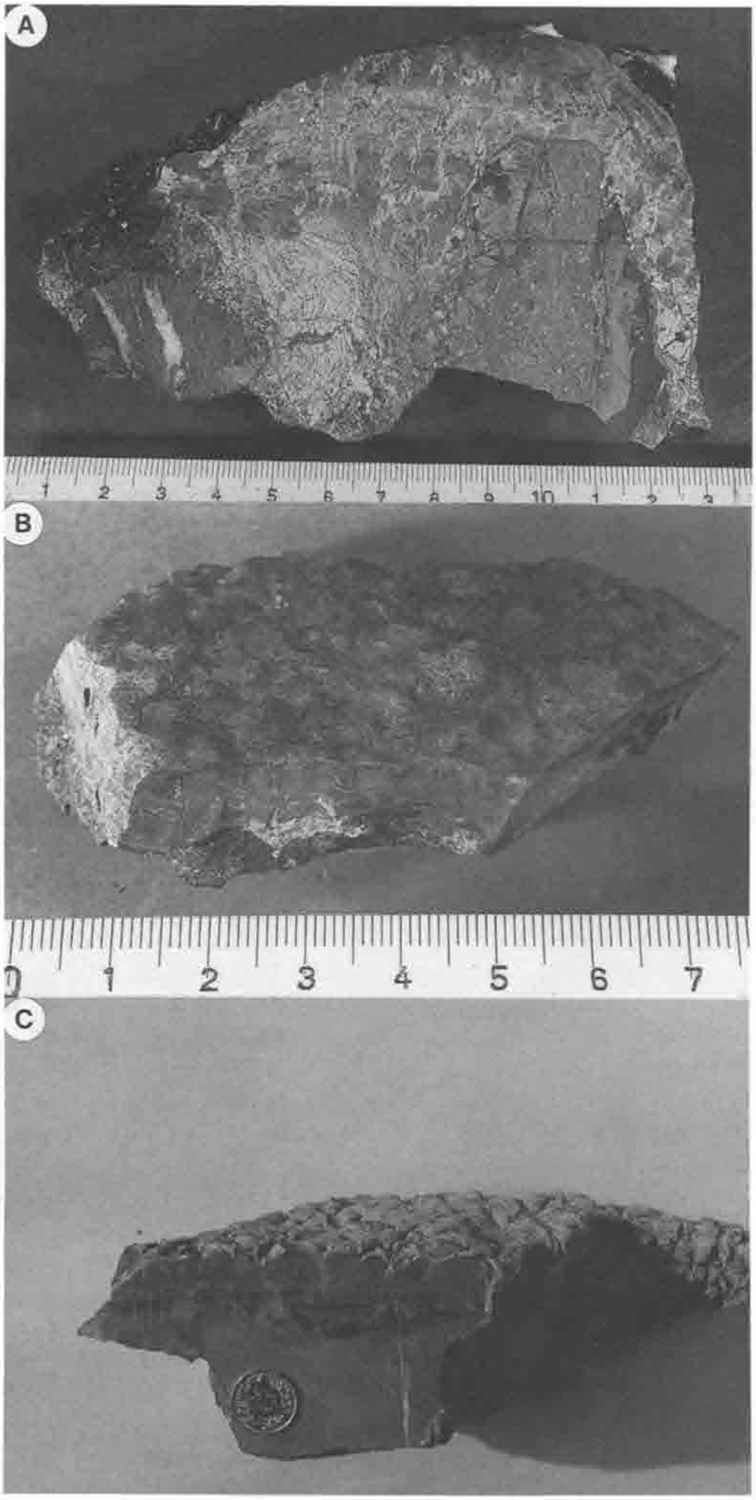
Microbes are generally considered to play an important role in interstitial phosphate enrichment and phosphogenesis (Cayeux, 1936; Riggs, 1979; Lucas and Prévôt, 1981, Lucas and Prévôt, 1984, Lucas and Prévôt, 1985; O'Brien et al., 1981; Soudry and Champetier, 1983; Krajewski, 1983, Krajewski, 1984; Zanin et al., 1985; Southgate, 1986; Soudry, 1987; Gächter et al., 1988; Soudry and Lewy, 1988, Soudry and Lewy, 1990; Prévôt et al., 1989; Hirschler, 1990; Hirschler et al., 1990; Lamboy, 1990a, Lamboy, 1990b; Lewy, 1990; Abed and Fakhouri, 1990; Prévôt, 1990; Reimers et al., 1990; Gächter and Meyer, 1993; Krajewski et al., 1994). Microbial decomposition of organic matter is instrumental in the delivery of dissolved phosphate to interstitial solutions. Most heterotrophic bacteria and fungi have the

Fig. 7. Pristine phosphatized coprolite in laminated organic-rich sediments of the mid-Triassic "Grenzbitumenzone" (Monte San Giorgio, southern Switzerland). The sediments of the Grenzbitumenzone are inferred to have originated below a stable anoxic water mass (Bernasconi, 1994) and the phosphatized particles resulted, for this reason, from phosphogenesis in anoxic sediments (coin diameter = 1.8 cm).

capability to hydrolytically break down organically bound phosphate using specific enzymes as catalysts (e.g., phosphatase, phytase, nucleotidase, etc.; Ehrlich, 1981). Furthermore, microbes appear to actively participate in metal redox cycles through the direct coupling of iron reduction with organic-carbon oxidation (e.g., Lovley and Phillips, 1988; Lazzaretti and Hanselmann, 1992; Krajewski et al., 1994). Microbes are also involved in dissolving francolite and other inorganic phosphates, as well as phosphate-bearing shells, skeletons, and fish hard parts ("microbial solubilization"). This is achieved through: (1) the production of inorganic and organic acids that attack the solid phosphates; (2) the production of chelators, such as 2-ketogluconate, citrate, oxalate, and lactate, that complex the cationic part of solid phosphates and thus force their dissolution; and (3) the production of H_2S, which may induce the reduction of iron oxyhydroxide and liberate phosphate associated with iron oxyhydroxide (Ehrlich, 1981; Burdige and Nelson, 1986; Krajewski et al., 1994).

Gächter et al. (1988) demonstrated the ability of microbes in fresh-water systems to rapidly release substantial amounts of phosphate upon transfer into anoxic waters (up to 25% of total microbial phosphate). Under oxic conditions, in environments in which dissolved phosphate is abundant, microbes tend to accumulate and store phosphate as the end product of oxidative phosphorylation (Toerien et al., 1990). Microbial phosphate release in anoxic media appears to be the consequence of shifting into an oxygen-independent mode of metabolism by activating an organic electron acceptor with energy stored in polyphosphate intracellular granules (Gächter et al., 1988). This microbial mechanism may be important in the redistribution of phosphate from anoxic into oxic zones and is thought to be crucial in the retention of dissolved phosphate in sediments under oxic conditions and release of interstitial phosphate to overlying bottom waters under anoxic conditions (e.g., Gächter and Meyer, 1993; Ingall et al., 1993, Ingall et al., 1994; Ingall and Jahnke, 1994; Van Cappellen and Ingall, 1994). It may also be instrumental in the rapid buildup of dissolved interstitial phosphate levels upon sudden burial of microbial assemblages by laterally dislocated sediments (Föllmi and Garrison, 1991) or through fluctuations in the redox boundary below microbial colonies at the sediment-water interface (Krajewski et al., 1994).

The exact role of microbes in francolite precipitation processes remains unclear (e.g., Ehrlich, 1981; Krajewski et al., 1994). It is evident that to a large extent, microbes are responsible for the chemical composition of pore waters and may thus indirectly promote francolite precipitation. However, direct and active participation of microbes in francolite precipitation and phosphate deposition in sediments has not yet been positively demonstrated, with the exception of the accumulation and storage of intracellular polyphosphate granules (e.g., Gächter et al., 1988; Konhauser et al., 1994). The often described occurrence of phosphatized microbes in offshore and onshore deposits is partly due to the resemblance of francolite rod-like crystallites and spindle-form microbes. Van Cappellen (1991) experimentally demonstrated that such crystallites can be grown in sea-water-like solutions under sterile conditions. On the other hand, good evidence exists for the preservation of phosphatized cellular microbes in experimental setups (Lucas and Prévôt, 1985) and ancient phosphorite deposits (Krajewski et al., 1994). The phosphatized microbes are preserved as capsules with apertures oriented towards open pore space (Krajewski et al., 1994), or as phosphatized filaments (e.g., Martín-Algarra and Vera, 1994; Vera and Martín-Algarra, 1994). In phosphorite deposits, the close relation between microbes and phosphogenesis is in many cases demonstrated by the occurrence of phosphatized stromatolites (Krajewski, 1983, Krajewski, 1984; Krajewski et al., 1994; Fig. 8). However, a cause-and-effect relationship cannot (yet) be deducted from the close association between phosphorites and preserved microbes or microbial colonies. The preserved microbial bodies may just as well have served as a passive substrate for inorganic francolite precipitation. Reconstructing a causal relationship is all the more difficult because phosphatized or phosphatizing stromatolites have not yet been identified in present-day natural environments. Promis-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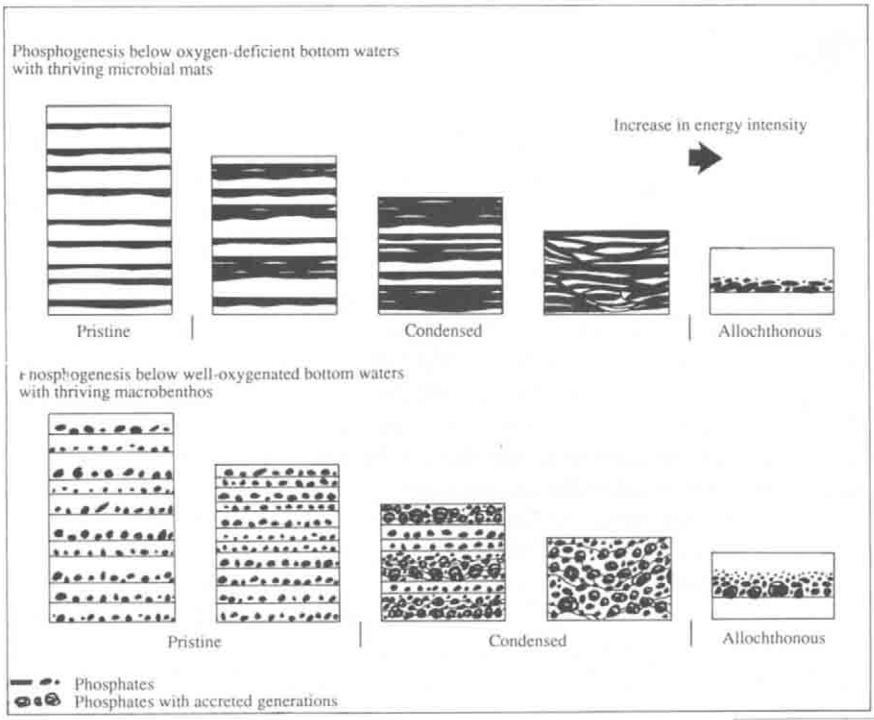


Fig. 9. Diagrammatic overview over different stratification types in sedimentary phosphorite as a function of energy levels in bottom waters and the corresponding degree of sediment reworking. Pristine, condensed and allochthonous phosphate stratification types are shown for particular and laminated deposits.

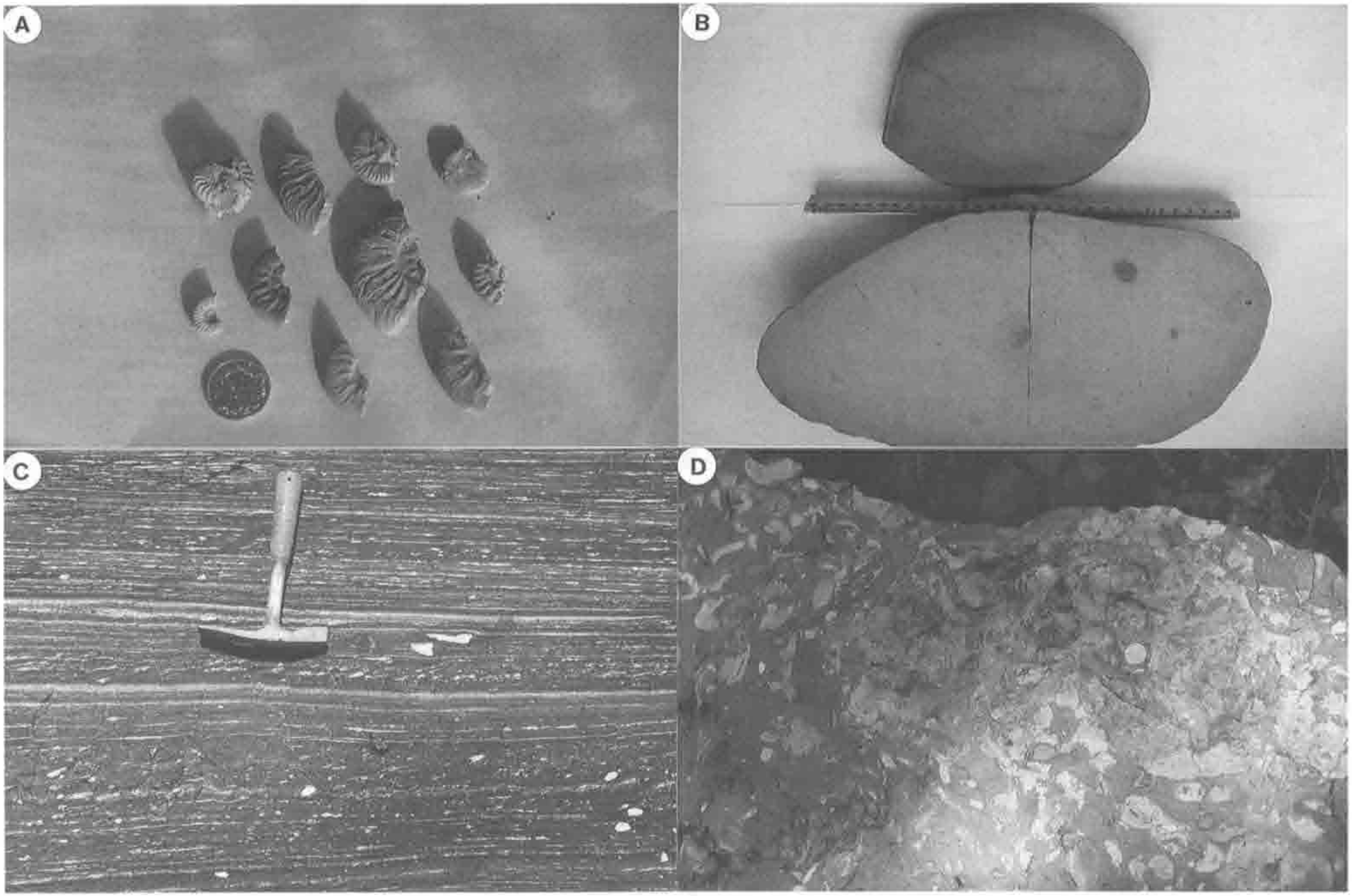
ing in this regard are experimental setups, in which microbial mats undergo phosphatization when levels of dissolved phosphate are sufficiently high (Krajewski et al., 1994).

4. Sedimentology of phosphorites

4.1. Stratification types

Once francolite is precipitated and phosphatic particles and laminae have formed, they may either be buried by subsequent sediments, transferred below the zone of main phosphogenesis and remain pristine, or experience sediment-reworking and become concentrated into phosphorite accumulations, depending on the presence and intensity of physical and biological sediment-reworking processes at the site of phosphogenesis, the sediment properties and the sediment-binding capacity of microbial colonies (Föllmi et al., 1991). Phosphatic particles are particularly prone to be concentrated by, for instance, winnowing processes, because of the high

Fig. 8. Examples of phosphatized microbial colonial structures preserved as stromatolites. (A) Phosphatized columnar stromatolite attached to reworked pebbles of shallow-water carbonate. Note tilted stock on the left side of the sample, overgrown by normally oriented microbial mats. Albian, quarry near Dornbirn (Vorarlberg, Austria; centimeter scale at the base; from Föllmi, 1989; reproduced with permission from Springer, Heidelberg). (B) Phosphatized columnar stromatolite. Albian, south of Ebnit (Vorarlberg, Austria; centimeter scale at the base; from Föllmi, 1989; reproduced with permission from Springer, Heidelberg). (C) Phosphatized columnar stromatolite. Lower Cenomanian, Alp Sellamatt (Churfirsten, eastern Switzerland; coin diameter = 1.8 cm; compare Ouwehand, 1987).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specific gravity of francolite (2.9 g/cm^3) relative to other sediment particles (1.5–2.5 g/cm^3). In general, we may distinguish between three different stratification types of phosphorites (Fig. 9; Föllmi et al., 1991; Föllmi and Garrison, 1991; Glenn et al., 1994b):

(1) *Pristine phosphate* (Figs. 7–10): The term pristine is applied to phosphates, which are autochthonous, have experienced one cycle of phosphogenesis, and lack signs of concomitant and/or subsequent sedimentary reworking such as winnowing, erosion and/or lateral transport. They typically consist of one single phosphate generation. Pristine phosphates occur as discrete phosphatized laminae and lenses, as phosphatic particles such as coated grains, coprolites, fossils and fossil debris and peloids (i.e., mm-sized structureless phosphatic particles), scattered throughout the sediment, or as discrete phosphatized areas (e.g., phosphatized burrow systems).

(2) *Condensed phosphate* (Figs. 11 and 12): Condensed phosphates are more or less autochthonous, but have experienced one or more phases of sediment winnowing and erosion ("Baturin cycles"), and may have gone through more than one cycle of phosphogenesis. In the case of several phases of phosphogenesis, condensed phosphates may exhibit various accreted phosphate generations, which are discerned by the presence of internal boundaries separating the phosphate phases (sometimes marked by borings or overgrown by serpulids and sessile arenaceous foraminifera), and the inclusion of different and/or differently sized detrital particles in the different phosphate generations. Condensed phosphatic beds which have experienced multiple phases of sediment reworking and phosphogenesis may display complex internal microstratigraphic relationships characterized by small-scale unconformities, low-angle truncations and scour marks. Intensely winnowed and reworked beds may lack an internal architecture, and consist of an amalgamate of heterogeneous phosphate particles, and/or include phosphatized fossil mixtures of different ages and ecological habitats (e.g., Föllmi, 1989).

(3) *Allochthonous phosphate* (Fig. 13): Allochthonous phosphates result from sedimentary reworking of originally pristine or condensed phosphates and subsequent lateral transport within sediment-carrying flows (induced by gravity, currents, storms, tides, earthquakes, etc.). Transported phosphates are recognized by features characteristic of redeposition, such as the presence of a sharp and erosive lower boundary, internal grading, and the mixing of phosphatic particles with non-phosphatic particles. Allochthonous phosphates may be derived from areas in which phosphogenesis is a still ongoing process, or from areas in which major phosphogenesis has terminated (reworking of "fossil" phosphates). In many cases, allochthonous phosphates document episodes of major phosphogenesis in areas which themselves are not accessible or are no longer preserved.

Pristine phosphates originate in sedimentary regimes characterized by minimal sediment-reworking, whereas condensed phosphates form in areas in which hydraulic energy levels were intermittently or persistently high and where sediment-accumulation rates are balanced by sediment-erosional rates. The presence of multiple phosphate generations in a complex internal microstratigraphic architecture is indicative of the effect of repetitive cycles of sediment burial, phosphogenesis and sediment reworking, i.e., "Baturin cycles", which are the result of fluctuations in the intensity of ambient bottom-water

Fig. 10. Examples of pristine phosphate occurrences: (A) Phosphatized ammonites preserved in a bioturbated muddy marl. Toarcian, Gross-Wolf, Staffelegg (Aargau, Switzerland; coin diameter = 1.8 cm). By courtesy of Mr. O. Kuhn, Zürich. (B) Large phosphatized nodules preserved in bioturbated hemipelagic marls. Maastrichtian or Danian, Bezmiechowa near Sanok (Outer Flysch Zone, S.E. Poland). By courtesy of Dr. K. Krajewski, Warsaw, Poland. (C) Light-colored phosphate-bearing laminae and lenses, intercalated with dark and organic-rich marly mud. Miocene, Naples Beach (W. Santa Barbara, California, USA; from Föllmi et al., 1991; reproduced with permission from Springer, Heidelberg). (D) Phosphatized burrow infills at the top of a calcarenite. Sinemurian, Frick (Aargau, Switzerland; coin diameter = 1.8 cm).

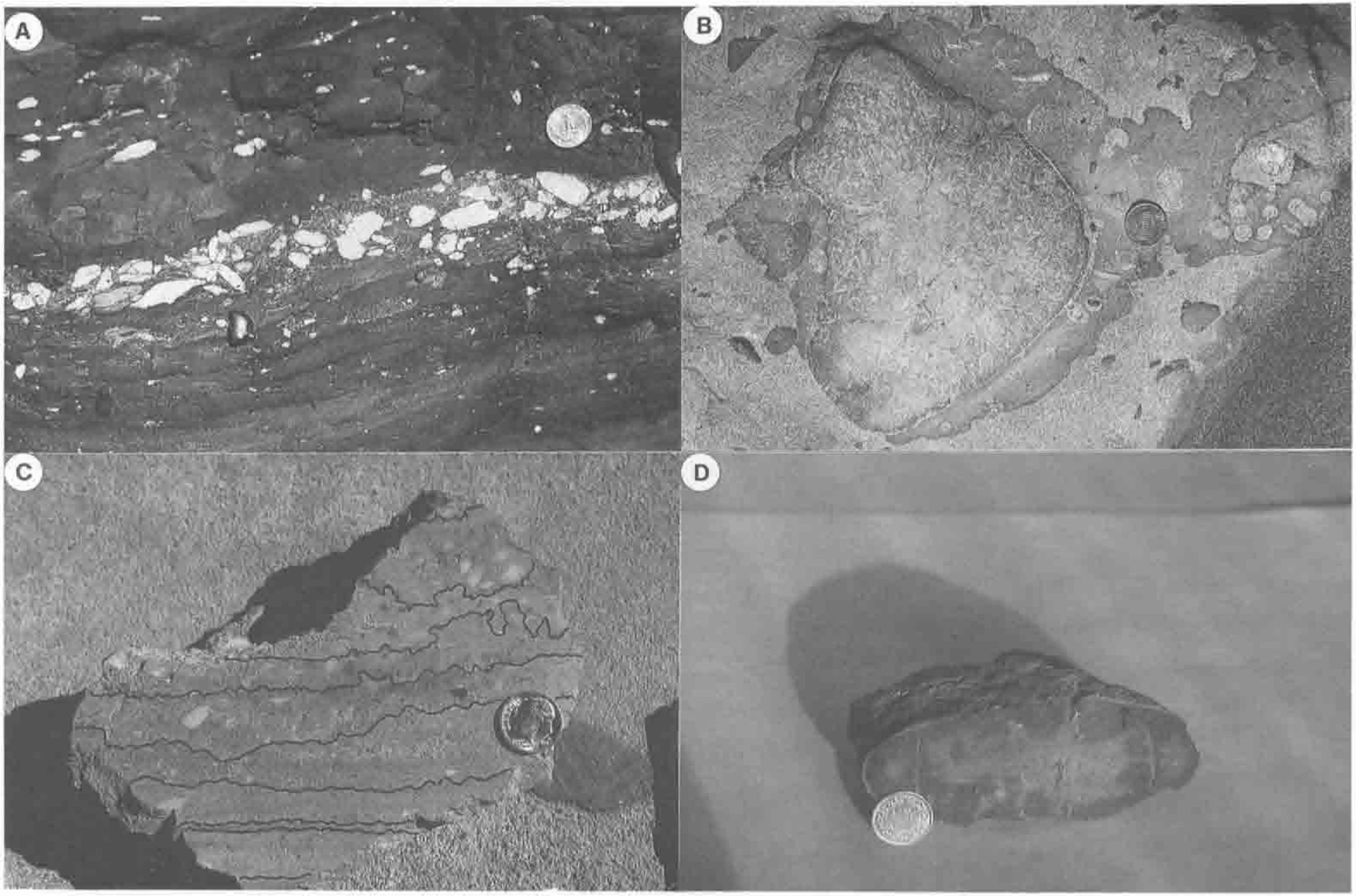
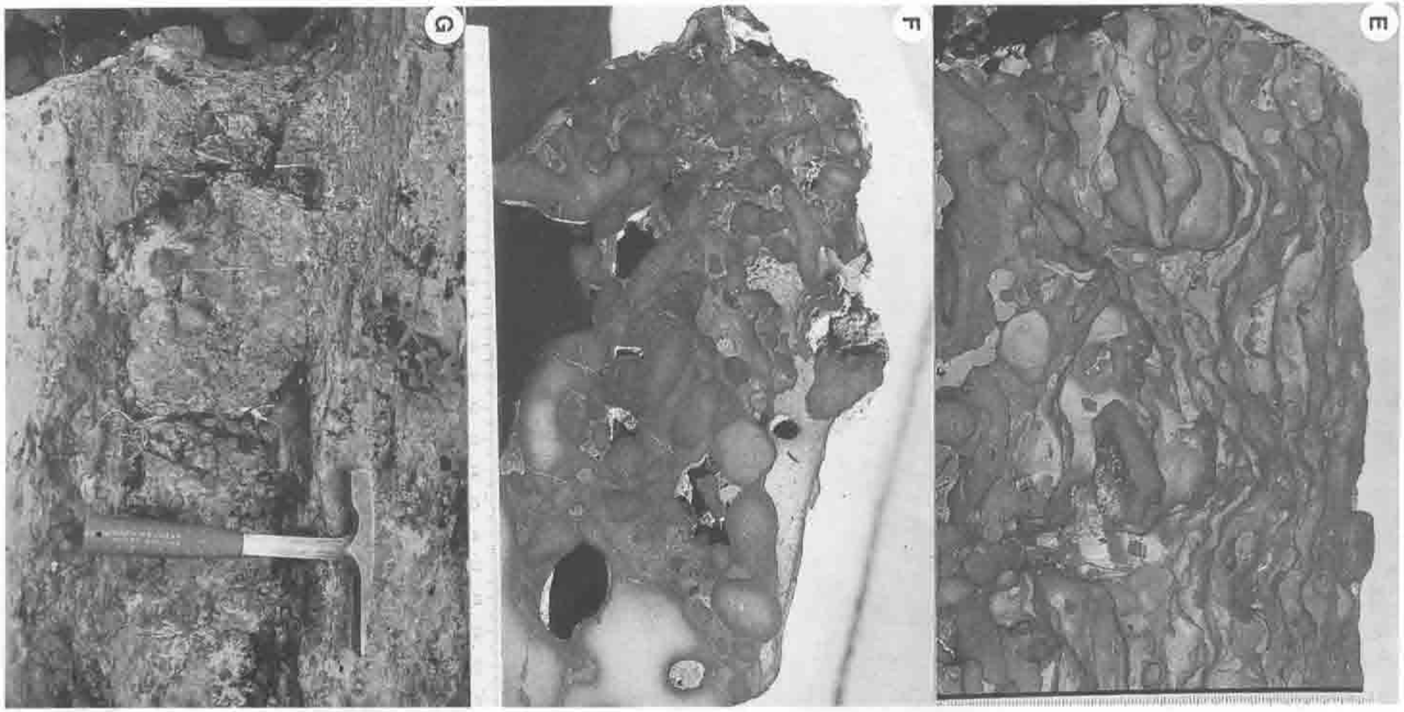
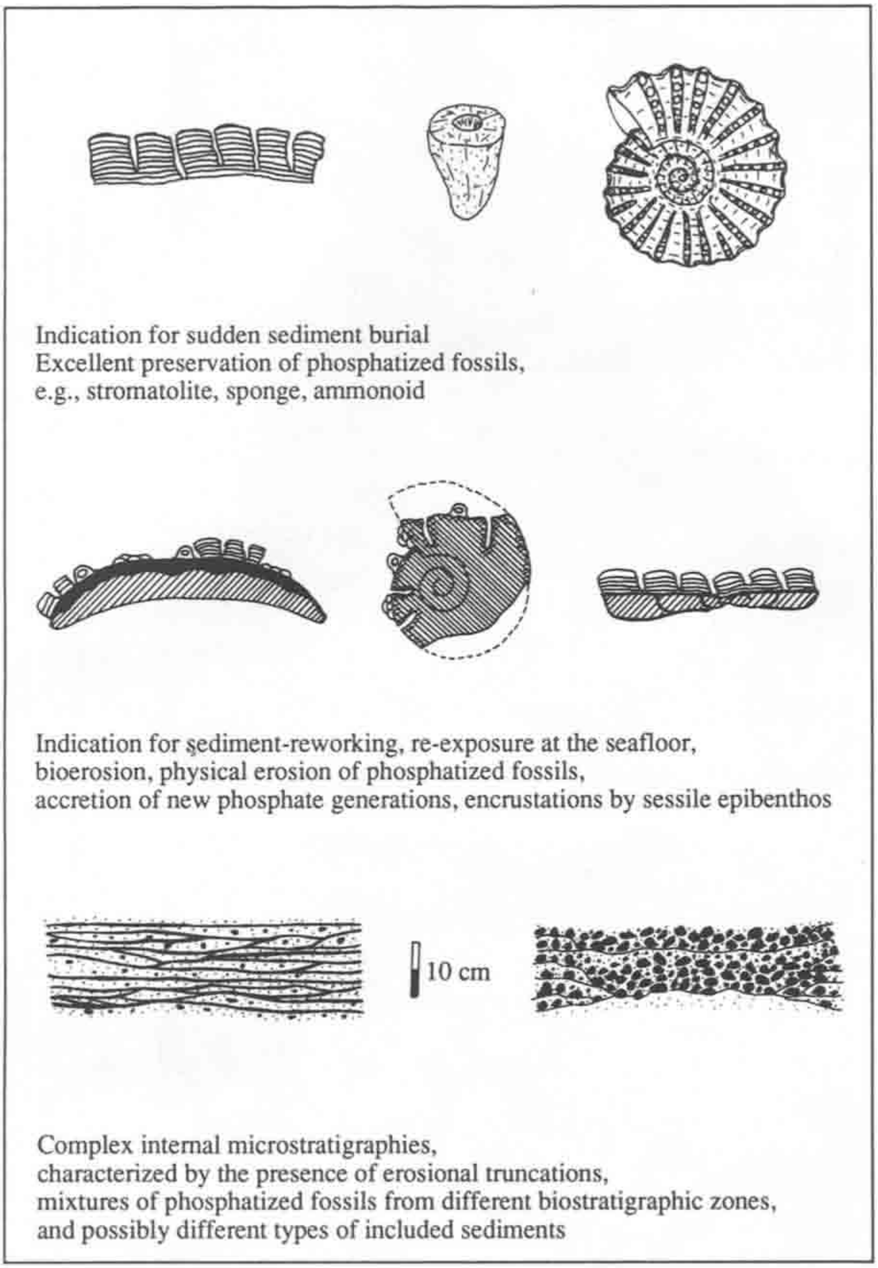


Fig. 11. Examples of condensed phosphate occurrences: (A) Winnowed and condensed interval enriched in light-colored phosphatized nodules, embedded in dark and organic-rich marly mudstone. Miocene, Naples Beach (W. Santa Barbara, California, USA; coin diameter = 2.4 cm; from Föllmi et al., 1991; reproduced with permission from Springer, Heidelberg). (B) phosphatized rim around whale vertebra embedded in a coarse-grained sandstone. Note pholad borings documenting a phase of reworking and re-exposure at the sediment–water interface after phosphogenesis. Pliocene, New Brighton Beach (E. Santa Cruz, California, USA; coin diameter = 1.9 cm; from Föllmi et al., 1991; reproduced with permission from Springer, Heidelberg). (C) Condensed bed including numerous internal erosive boundaries (marked on the photo). The distinct coarsening upward trend of the phosphatized particles suggests that a series of winnowing events of increasing strength may have been instumental in the formation of this bed (compare Föllmi et al., 1991). Miocene, Naples Beach (W. Santa Barbara, California, USA; coin diameter = 1.7 cm; from Föllmi et al., 1991; reproduced with permission from Springer, Heidelberg). (D) Surface of a cut and polished phosphatic nodule showing scratches produced by crustaceans. The crustacean traces document the reworked character of this nodule. Eocene, Friedland (Neu-Brandenburg, Germany; coin diameter = 1.8 cm). By courtesy of E. Herrig, Greifswald, Germany.



(E) Condensed laminated bed. Note the erosive, irregular, and often discontinuous character of the laminae, which, in their stacking pattern, resemble stromatolite buildups. Intervening sediment is a silty mudstone. Miocene, float clast from Naples Beach (W. Santa Barbara, California, USA; centimeter scale to the right; compare Föllmi and Garrison, 1991; Föllmi et al., 1991). (F) Condensed phosphatized bed including allochthonous phosphatized particles. Note the irregularity of the boundaries between different generations of phosphatized sediment. Miocene–Pliocene boundary, Lompoc (Santa Maria, California, USA; centimeter scale at the base). (G) Condensed phosphatic bed. Bed is amalgamated and include mixture of ammonites from different biostratigraphic time zones. Valanginian–Hauterivian, Obersäss (Churfirsten, Switzerland). By courtesy of Mr. O. Kuhn, Zürich.

energy levels. This sedimentary regime is typical for marine environments of major phosphorite formation (compare Section 3.4.). Allochthonous phosphates are the result of short high-energy pulses during which pristine or condensed phosphates become re-exposed at the sediment–water



Indication for sudden sediment burial
Excellent preservation of phosphatized fossils,
e.g., stromatolite, sponge, ammonoid

Indication for sediment-reworking, re-exposure at the seafloor,
bioerosion, physical erosion of phosphatized fossils,
accretion of new phosphate generations, encrustations by sessile epibenthos

Complex internal microstratigraphies,
characterized by the presence of erosional truncations,
mixtures of phosphatized fossils from different biostratigraphic zones,
and possibly different types of included sediments

Fig. 12. Taphonomical and sedimentological characteristics of condensed phosphatic beds. Good preservation of fossils in condensed intervals may point to the effect of rapid burial and consequent phosphogenesis. The presence of abraded or eroded and encrusted phosphatic particles and fossils indicates the effect of prolongated re-exposure at the sea floor after phosphatization.

interface, disrupted, and dislocated in offshore or longshore directions.

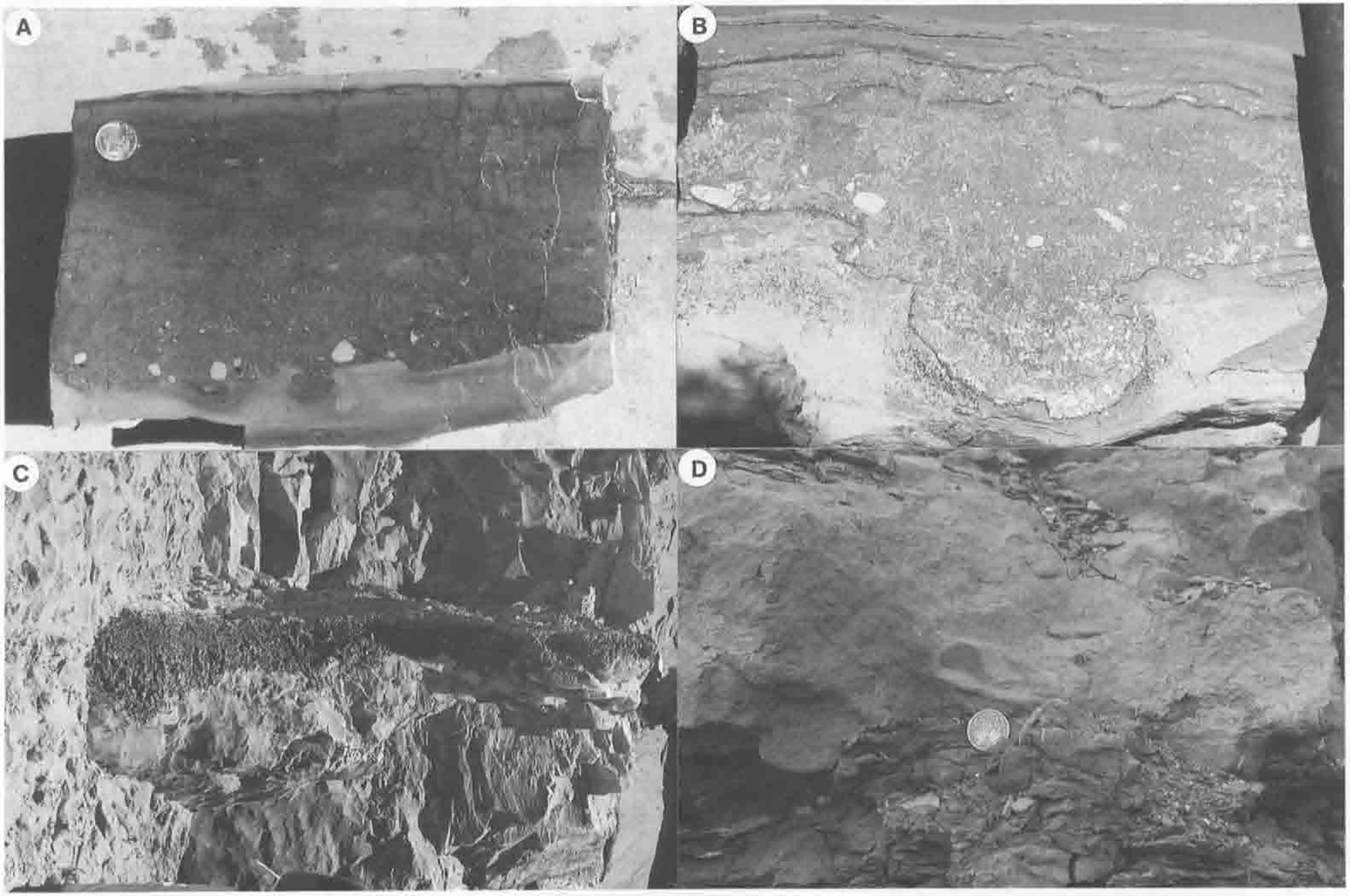
Stratification hybrids, i.e., superposition and intertwining of different phosphate stratification types are possible and common in phosphorite deposits. For instance, condensed phosphatic beds may include fractions of allochthonous phosphate particles and may be topped by a pristine phosphate lamina (e.g., a phosphatized stromatolite). Changes in stratification types may also be observed in single phosphate horizons along lateral transects (e.g., Fig. 14). Such transitions show that the above listed stratification types are end-members of a natural continuum of sediment structures which are controlled by spatial and temporal changes in the sedimentary regime and hydraulic energy levels.

4.2. Phosphatic sediments and the reconstruction of ancient sedimentological and environmental regimes

The occurrence of phosphorites in ancient sedimentary realms is valuable in the reconstruction of the sedimentary, biogeochemical and environmental regime prevalent at the time of deposition. The distribution, type of phosphatization, type of stratification, type of preserved phosphatized ecosystem, degree of condensation and time span of phosphogenesis are all indicative of environmental conditions under which phosphorite formation occurred. The synsedimentary/early diagenetic timing of phosphogenesis, and the microcrystallinity and low solubility of francolite once formed, render phosphorite a first-class medium for the preservation of sedimentological and environmental signals. Radiogenic and stable isotope values (e.g., Sr, Nd, U, S, O, C) and rare-earth distribution in phosphorites may in many cases be interpreted as sea-water signatures (this seems especially true for phosphatized laminae and crusts which formed near the sediment–water interface; e.g., Piper, 1994). Preserved phosphatized ecosystems give valuable indications of bottom-water oxygen and nutrient contents, and the character of colonized substrate (e.g., hardground epibenthos, shallow-burrowing bivalves, bioturbation). In francolite, important guide fossils may be preserved, which are otherwise less stable under normal diagenetic conditions (e.g., radiolarians, diatoms). The type and distribution of phosphate stratification types give valuable information on the presence and intensity of hydraulic energy.

In the following, an ancient, onshore phosphate-bearing sedimentary deposit will be used to illustrate the above. The succession of interest is the Aptian–Cenomanian Garschella Formation that was deposited along the northern Tethyan passive margin (Delamette, 1985, Delamette, 1988, Delamette, 1990; Föllmi, 1986, Föllmi, 1989, Föllmi, 1990; Föllmi and Ouwehand, 1987; Ouwehand, 1987; Föllmi et al., 1994). Proximal occurrences (with respect to the paleo-shoreline) of the Garschella Formation consist predominantly of glauconitic sandstones and marls, which include up to five distinguishable and clearly defined condensed phosphatic beds. In a shoreward direction, the phosphatic beds tend to grade into less condensed and thicker glauconitic sediments, whereas in seaward directions, the phosphatic beds tend to bundle and merge into one single, strongly condensed phosphatic bed (net sediment accumulation rates were 2–20 cm/Myr during several million years; Fig. 14). Beyond a pronounced mid-shelf edge (which closely corresponds to the distal edge of the underlying, drowned, Barremian to Lower Aptian carbonate platform), sediments of the Garschella Formation consist primarily of channel-infills and fan deposits. These include reworked and displaced, inner-shelf derived sediment including allochthonous phosphorites. In distal directions, Garschella sediments pass into fine-grained, organic-rich, marl- and claystones (Fig. 14).

The distribution of phosphate stratification types, the proximal-distal trends in condensation, the presence/absence of bioturbation, and the character of phosphatized organisms suggest a sedimentary regime that is characterized by a powerful and persistent, east–west directed longshore current system near the upper boundary of an oxygen-minimum zone (Föllmi and Delamette, 1991). The zone of maximum condensation along the distal inner shelf can be traced along large parts of the northern Tethyan margin, and is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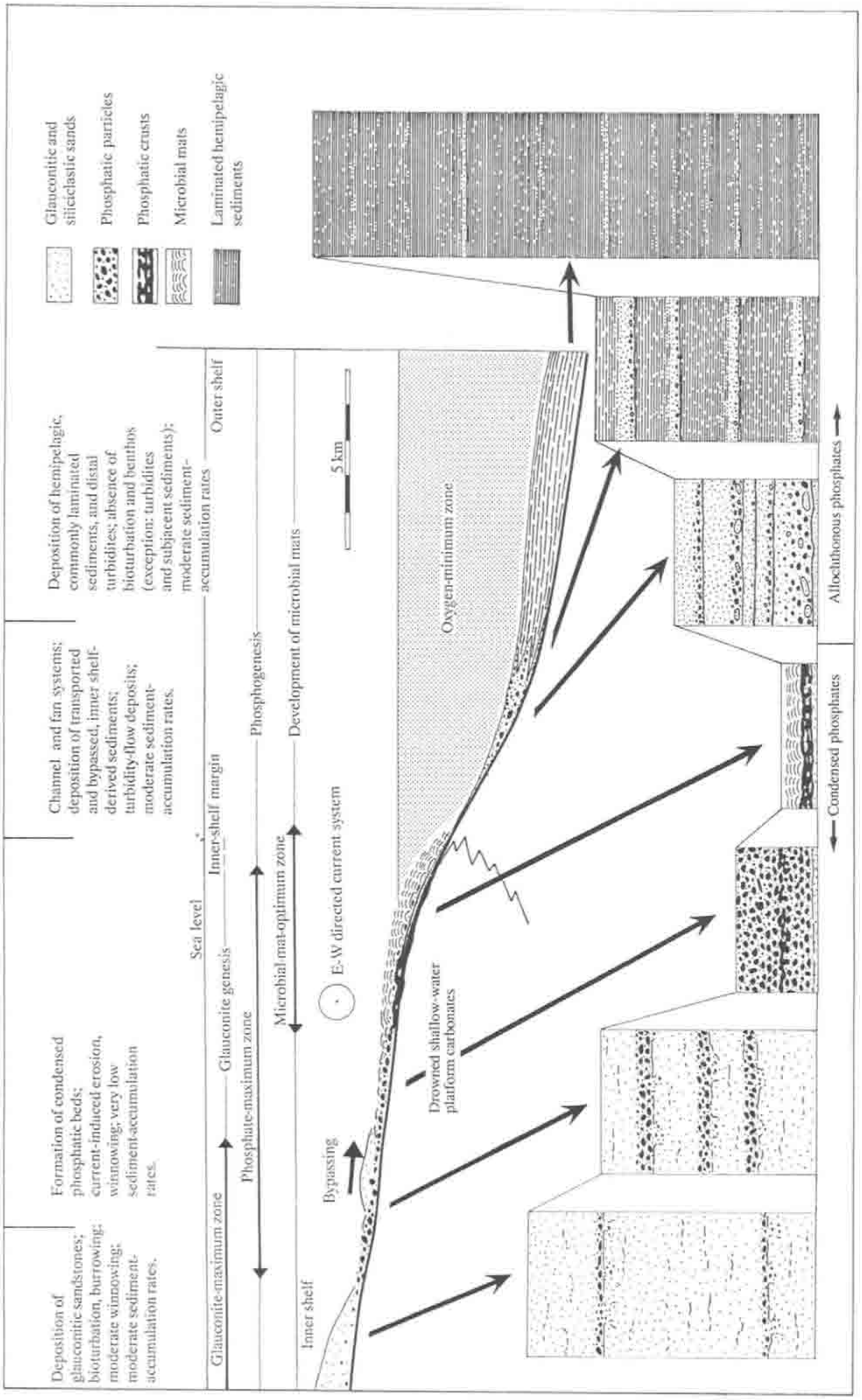
thought to have coincided with the paleoposition of the current axis. Spatial shifts in this zone of maximum condensation through time may document up- and down-slope shifts in the current position. The channel and fan deposits along the mid-shelf ramp have been interpreted as "spillover", bypassed, sediments, derived from the inner shelf (Fig. 14). The presence of multiple phosphate generations in the condensed phosphatic beds of the Garschella Formation, the overgrowth of phosphate surfaces by encrusting organisms, the complex internal microstratigraphies of the condensed beds characterized by the presence of truncated layers, rapid lateral changes in sediment type, and lenticular bedding demonstrate the effect of repetitive Baturin cycling, due to current-induced, episodic, sediment bypass. Notably, most of the sedimentary and environmental characteristics in this reconstructed sedimentary regime are also observed in marine areas of modern phosphogenesis and phosphorite formation (compare Section 3.4.).

4.3. Phosphorite and sea-level change

The distribution of phosphorites in sedimentary successions is not random, and their occurrences are often predictable. Early workers on phosphorites noted a preferential coincidence of phosphorites and major lithological changes, unconformities and hiatuses, and related this to major changes in ecology, environment, current systems, climate and sea level (e.g., Murray and Renard, 1891; Collet, 1906; Grabau, 1919; Heim, 1924, Heim, 1934, Heim, 1958; Heim and Seitz, 1934; Schaub, 1936, Schaub, 1948). In more recent publications, major occurrences of (condensed) phosphorite have more specifically been tied to transgressive successions and correlated with periods of relative sea-level rise (e.g., Sheldon, 1980; Arthur and Jenkyns, 1981; Baturin, 1982; Riggs, 1984; Cook et al., 1990; Glenn and Arthur, 1990; Riggs and Sheldon, 1990). A twist to this is the general notion that, although major phases of phosphogenesis may coincide with major sea-level rise, subsequent reworking and concentration of phosphatic particles into phosphorites may occur during relative sea-level highstand or subsequent sea-level fall (e.g., Bushinski, 1966; Baturin, 1971a, Baturin, 1982; Riggs, 1984; Glenn and Arthur, 1990; Jarvis, 1992; Compton et al., 1993; compare also Trappe, 1992).

With the development of reflection seismics as a tool to monitor subsurface sedimentary architectures and the advent of sequence stratigraphy to interpret depositional geometries, phosphorites are commonly used as marker horizons, indicating marine or maximum flooding surfaces, i.e., surfaces formed during maximum sea-level rise (e.g., Loutit et al., 1988; Föllmi et al., 1992; Compton et al., 1993; Glenn et al., 1994b; compare also Hiatt, 1994). Phosphorites bound to marine or maximum flooding surfaces are typically condensed, but may include portions of pristine and allochthonous phosphates. They mark major sedimentary changes, especially if lowstand deposits or lowstand-systems tracts are lacking and the flooding surface coincides with a (para-)sequence boundary (Fig. 15). Sets of parasequences separated by condensed phosphatic beds within transgressive systems tracts typically show a retrogradational stacking pattern with the con-

Fig. 13. Examples of allochthonous phosphate occurrences: (A) Phosphatic gravity-flow deposit including phosphatized coated grains showing distinct grading and non-phosphatized rip-up clasts. Embedded in a pelagic opal C–T porcelanite. Miocene, Carmel Valley Road (California, USA, Coin diameter = 1.9 cm; compare Garrison et al., 1987; Föllmi et al., 1991). (B) Gravity-flow deposit consisting of phosphatized particles and non-phosphatized rip-up clasts, embedded in a non-phosphatic, hemipelagic, mudstone. Note the scoured surface at the base. Oligocene, San Isidro (Baja California, Mexico; compare Grimm and Föllmi, 1994). (C) Gravity-flow deposit consisting of phosphatized particles and pebbles, embedded in hemipelagic siliceous mudstone. The phosphatized pebbles show complex internal architectures suggesting an origin from a condensed bed related to the ones depicted in Fig. 11 (E and F). Miocene–Pliocene boundary, Mussel Rock (W. Santa Maria, California, USA; from Föllmi and Garrison, 1991; reproduced with permission from Academic Press, London). (D) Phosphatic gravity-flow deposit embedded in hemipelagic mud. Note the presence of *Thalassinoides* burrows at the base. Campanian, Abu Tartur (Egypt; (coin diameter = 2.4 cm); compare Föllmi and Grimm, 1990; Grimm and Föllmi, 1994; Föllmi, 1995b).


Deposition of glauconitic sandstones; bioturbation, burrowing; moderate winnowing; moderate sediment-accumulation rates.
Formation of condensed phosphatic beds; current-induced erosion, winnowing; very low sediment-accumulation rates.
Channel- and fan systems; deposition of transported and bypassed, inner shelf-derived sediments; turbidity-flow deposits; moderate sediment-accumulation rates.
Deposition of hemipelagic, commonly laminated sediments, and distal turbidites; absence of bioturbation and benthos (exception: turbidites and subjacent sediments); moderate sediment-accumulation rates
Glauconitic and siliciclastic sands
Phosphatic particles
Phosphatic crusts
Microbial mats
Laminated hemipelagic sediments
Glauconite-maximum zone
Glauconite genesis
Sea level
Inner-shelf margin
Outer shelf
Inner shelf
Phosphate-maximum zone
Phosphogenesis
Microbial mat-optimum zone
Development of microbial mats
E-W directed current system
Bypassing
Drowned shallow-water platform carbonates
Oxygen-minimum zone
5 km
Condensed phosphates
Allochthonous phosphates

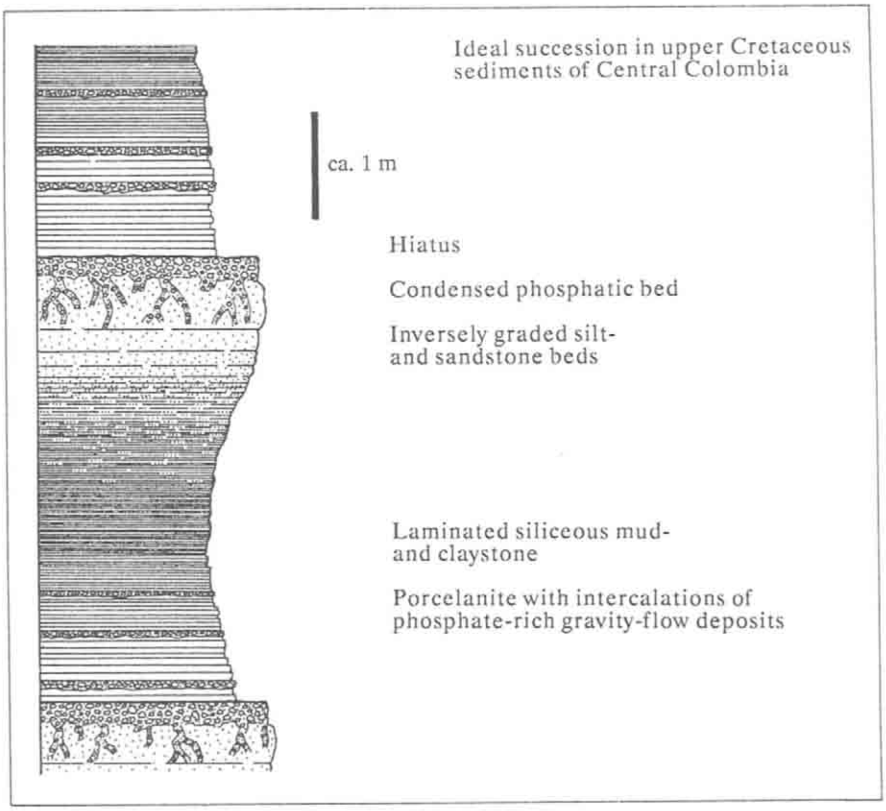
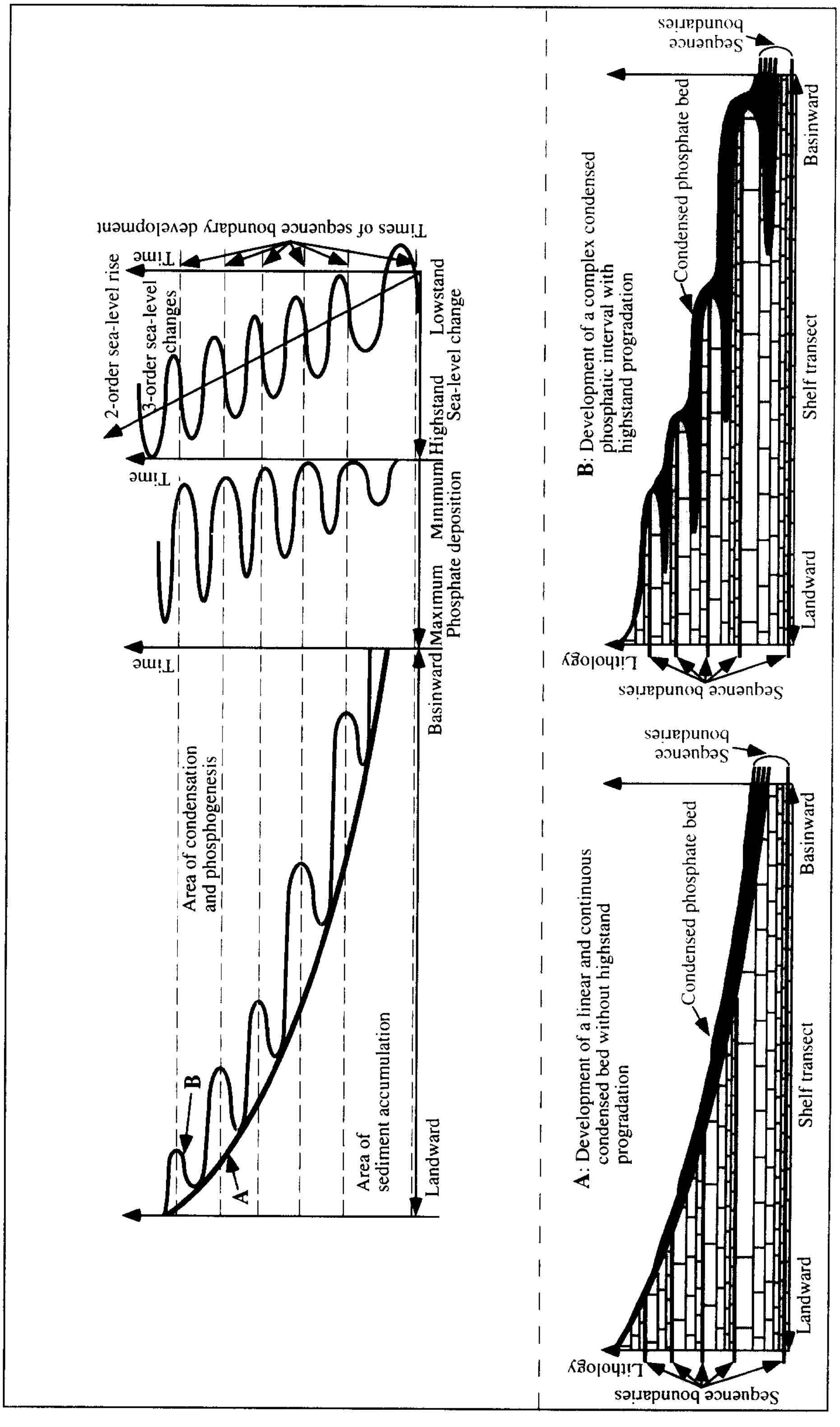


Fig. 15. Idealized succession in Upper Cretaceous sediments of Central Colombia, consisting of a well-developed coarsening-upward succession, topped by a condensed phosphatic bed. The succession is interpreted as a parasequence with the coarsening upward portion representing a shallowing upward phase and the condensed phosphatic bed representing a deepening upward phase. The interface between the condensed phosphatic interval and the overlying coarsening upward succession coincides with maximum flooding during this high-frequency cycle. The allochthonous phosphates within the basal, hemipelagic, portion of the overlying coarsening upward sequence were reworked during late stages of relative sea-level rise or early sea-level highstand (from Föllmi et al., 1992; reproduced with permission from Elsevier, Amsterdam).

densed phosphate intervals being arranged in an onlap pattern (e.g., Van Wagoner et al., 1988). Phosphorites subsequently reworked from occurrences associated with flooding surfaces are usually allochthonous and may be present in superposed highstand systems tracts, lowstand-systems tracts, or shelf-margin systems tracts. Allochthonous phosphorites in highstand systems tracts (or in the corresponding shallowing-upward succession of parasequences) consist chiefly of phosphate particles without significant admixtures of non-phosphatic lithoclasts and are usu-

Fig. 14. Transect along the distal inner and proximal outer shelf of the northern Tethyan margin during the mid-Cretaceous (Garschella Formation). Note positions and different characters of the sediment deposits, different types of stratification in the phosphate horizons, and increase in condensation towards the mid-shelf margin (tracing the former margin of a drowned carbonate platform). Sediment distribution along this transect was determined by the position of a bottom-hugging, shelf-parallel current system. The lithologic logs are representative for the different settings on the shelf and approximately time-equivalent (slightly modified from Föllmi, 1989, Föllmi, 1990).


Times of sequence boundary development
2-order sea-level rise
3-order sea-level changes
Time
Time
Time
Lowstand
Highstand
Sea-level change
Minimum
Maximum
Phosphate deposition
Basinward
Landward
Area of condensation and phosphogenesis
Area of sediment accumulation
A
B
B: Development of a complex condensed phosphatic interval with highstand progradation
Condensed phosphate bed
Sequence boundaries
Sequence boundaries
Lithology
Landward
Shelf transect
Basinward
A: Development of a linear and continuous condensed bed without highstand progradation
Condensed phosphate bed
Sequence boundaries
Sequence boundaries
Lithology
Landward
Shelf transect
Basinward

ally embedded in (hemi-)pelagic sediments. Allochthonous phosphates in lowstand or shelf-margin systems tracts may contain significant admixtures of non-phosphatic lithified lithoclasts derived from subaerially exposed and lithified surfaces, and are usually embedded in detrital-rich sediments. Exceptions to these pattern are likely to occur; for instance when powerful currents rework condensed horizons plus underlying, lithified, sediments during relative sea-level highstands.

Environmental conditions that promote the formation of condensed horizons can be persistent and may last as long as several million years, thereby encompassing more than one major cycle of relative sea-level change (Föllmi et al., 1994). This is especially the case if long-term sea-level change is directed toward sea-level rise and shorter term sea-level changes only modulate this trend (Fig. 16). In this case, sediment supply to outer-shelf and slope segments is usually low and the outer-shelf sequences are sediment-starved. If, in such a situation, longshore currents are present and powerful enough to induce sediment bypass, then conditions are created for the formation of strongly condensed intervals. Condensed phosphatic beds that have formed under such conditions typically consist of an amalgamate of phosphates of different ages, formed during different phases of long-term sea-level rise. Such beds may split into different, separated, beds towards proximal, landward, directions, each bed tracing a flooding surface (Figs. 14 and 16). This is the case if the proximal zone of condensation episodically received sediments from more proximal areas, for instance during highstand progradation (Fig. 16). "Supercondensed" beds formed during several sea-level cycles are commonly diachronous at the base, with the oldest portions being located in the most distal parts of the depositional area. This is due to the onset of condensation in distal parts and a dislocation of the zone of condensation towards more proximal parts resulting in a diachronous "onlap" of the condensed bed. Termination of condensation, however, may be synchronous in the entire depositional system, if the long-term trend of sea-level rise ceased (e.g., Föllmi et al., 1994).

5. The environmental importance of phosphorus

5.1. Interactions of phosphorus and other biophile elements

The role of phosphorus as an important regulator of growth and reproduction, i.e., of biological productivity is widely acknowledged; its efficiency as a limiting factor, however, is still under investigation and depends on its availability relative to other nutrients such as nitrate, iron, or even CO_2, on the availability of trace elements, as well as on the physiological specifics of the biological community under consideration (e.g., Smith, 1984; Codispoti, 1989, Codispoti, 1994; Martin, 1991; Chisholm, 1992; Falkowski et al., 1992). Today, phosphate appears to have limiting functions in restricted shallow-marine areas (e.g., Shark Bay: Smith and Atkinson, 1984; Bothnian Sea: Granéli et al., 1990; Rosenberg et al., 1990; eastern Mediterranean Sea: Krom et al., 1991; Florida Bay: Fourqurean et al., 1992; Mississippi River delta: MacRae et al., 1994; Sargasso Sea: Cotner et al., 1994), in freshwater lakes (e.g., Schindler, 1977; Hecky and Kilham, 1988; Caraco et al., 1989) and pastoral and agricultural ecosys-

Fig. 16. Theoretical time–space and lithology–space diagrams in which the development of a strongly condensed, diachronous, phosphatic bed under conditions of long-term sea-level rise modulated by shorter term sea-level change is shown. *A* represents the development of a linear and continuous condensed horizon without intervening highstand progradation of sediments, whereas *B* depicts the development of a complex condensed phosphatic interval affected by intervening deposits of highstand progradational sediments. Note the decrease in the number of sequence boundaries merged in the condensed phosphatic interval in landward directions. They migrate proximally out of the condensed phosphatic interval and enter the adjacent, less condensed, sedimentary succession (modified after Föllmi et al., 1994).

tems (e.g., Smith, 1992; Crews, 1993). According to Holland (1978), Broecker and Peng (1982), Berner et al. (1993) and Mackenzie et al. (1993), phosphate may generally exert limiting functions in large parts of the living biosphere, because of the essentially unlimited availability of atmospheric nitrogen (i.e., phosphate becomes limiting over longer time periods, enveloping the more rapid fluctuations in the availability of nitrogen species; Mackenzie et al., 1993) and/or because of its capacities to regulate nitrogen-fixation processes (in terrestrial environments; Smith, 1992).

In its capacity as an essential nutrient, phosphate interacts with other biophile elements, such as carbon and oxygen. In the simplified formula of photosynthesis and its reverse — respiration (for marine plankton):

$$106CO_2 + 16HNO_3 + 2H_2SO_4 + H_3PO_4 + 120H_2O \leftrightarrow C_{106}H_{263}O_{110}N_{16}S_2P + 141O_2 \qquad (15)$$

each phosphorus atom drives the transformation of 106 carbon atoms and 141 oxygen molecules through primary productivity, under optimal conditions and using the Redfield ratio (Redfield et al., 1963; Stumm, 1973; Mackenzie et al., 1993). For comparison, in marine benthic microbial mats, the C/P molar ratio may be significantly lower and reach values between 30 and 65 (Reimers et al., 1990; Berner et al., 1993); in terrestrial vegetation, this ratio may be as high as 800 (Delwiche and Likens, 1977; Berner et al., 1993).

Transfer rates along important exogenic routes in the carbon cycle are forced by productivity through the uptake of atmospheric CO_2, export production and burial of organic matter (e.g., Garrels et al., 1975; Shaffer, 1989). In addition, productivity and carbon-burial rates are important regulating ingredients in the production and consumption of oxygen and other biophile elements (e.g., Holland, 1978; Kump, 1988; Berner and Canfield, 1989; Mackenzie et al., 1993). Phosphate exerts a driving and regulating influence on these processes, to an extent which is dependent on its function as a limiting nutrient in the ecological community under consideration.

5.2. Anthropogenic acceleration of the global phosphorus cycle

The exponential increase in phosphate exploitation rates from igneous and sedimentary sources and its use in fertilizers in agriculture, as well as in detergents and other chemical compounds employed in industry and households affects the global phosphorus cycle in a progressively increasing way (Stumm, 1973; Lerman et al., 1975, Sheldon, 1982; Caraco, 1993). Presently, the anthropogenic share in total flux rates of phosphate from continents into the marine reservoirs amounts to approximately 13.5×10^{12} gP/yr, which is more than 60% of the total flux (Froelich et al., 1982; Froelich, 1984; compare also Meybeck, 1982, Meybeck, 1993; Fig. 1). Regionally, in aquatic systems near heavily industrialized and populated centers, the anthropogenic share in phosphate flux rates is distinctively higher and reaches levels 10–100 times greater than pre-industrial levels (e.g., Caraco, 1993). The high rates of phosphate loading in these regions severely affect ecosystems, favoring opportunistic species and causing widespread retreat of formerly indigenous species. In many lakes, an increase in phytoplankton productivity (algal blooms) is observed, that causes seasonal or stable dysaerobic and anaerobic conditions and increased storage rates of organic matter in sediments. Similar trends are observed in the Baltic and North Sea, in the Gulf of Mexico, as well as in other peripheral seas (e.g., Baden et al., 1990; Ortner and Dagg, 1995). In tropical marine regions, complex and delicately balanced coral-reef ecosystems experience severe damage. Among probable causes discussed in the literature are increased phosphate and other nutrient influx rates (e.g., Red Sea reefs, Great Barrier Reef, Caribbean reefs and Hawaiian reefs; e.g., Hallock and Schlager, 1986; Hallock, 1987; Flanagan, 1993).

The present high phosphate influx rates coupled with enhanced influx rates of other nutrients increasingly impact marine, lacustrine, and continental ecosystems. Some of the possible consequences are (e.g., Nixon, 1993):(1) Severe damage to complex marine oligotrophic benthic ecosystems like coral reefs; (2) Limitation of marine and lacustrine benthic communities in general because of the possible development of dysaerobic bottom-water conditions; (3) Shorter feeding networks; (4) Simplified ecosystems; (5) Change to opportunistic phytoplankton species; (6) Increase in intensity and frequency of "red tides", i.e., toxic blooms of dinoflagelates and other planktic algae; (7) Toxic blooms of benthic cyanobacteria; (8) Higher rates of primary productivity; (9) Extensive colonization of the marine and lacustrine sediment–water interface by benthic microbial communities; (10) Increased burial rates of terrestrial, lacustrine and marine organic matter; (11) Focused redox boundaries at the sediment–water interface

A combination of these factors may affect the diversity and alter the composition of ecosystems on a global scale, if a persistent increase in levels of bioavailable phosphate occurs (on time scales of 0.1–1 kyr or longer). It is also most likely that this has happened during certain episodes in earth's history, as will be shown below (Section 5.5.).

5.3. Ecological coupling between the carbon and phosphorus cycles

The above list of ecological changes driven by eutrophic conditions suggests a profound impact of phosphorus loading on the exogenic, biologically mediated portion of the global carbon cycle. Under conditions of increased phosphate input rates, plankton production will increase linearly only until a point is reached where other nutrients become limiting (e.g., Martin, 1991). After this point, the productivity gradient may flatten out. At a certain level of eutrophication, the extant planktic ecosystem may not longer be stable and members of the system may be replaced by more opportunistic ones (e.g., foraminifera-dominated planktic ecosystem → diatom-dominated planktic ecosystem → dinoflagelate-dominated planktic ecosystem). These changes in the composition of plankton may also affect rates of productivity. The coupling of the phosphorus and carbon cycles in times of an accelerated phosphorus cycle appears, for this reason, to be nonlinear and partly unpredictable. This needs to be accounted for in numerical approaches modeling the interaction of these cycles (Föllmi et al., 1993).

Eutrophic conditions may suppress carbonate production in pelagic planktic communities and in shallow-water reefal communities and favor the export production of organic matter (see Sections 5.2. and 5.5.), thereby enlarging the ratio of exported organic carbon to carbonate carbon. This ratio is important to the carbon cycle because it influences the rate and efficiency with which CO_2 is stored in deep seas or in sediments (e.g., Berger and Keir, 1984; Archer and Mayer-Reimer, 1994). In Earth's history, this ratio appears to have fluctuated as a response to higher phosphorus flux rates and higher productivity. For instance, during the last glacial maximum, the decrease in atmospheric CO_2 may have been linked to an increase in the ratio of organic carbon to carbonate carbon that reached the sea floor, which, in turn, may have been dependent on changes in oceanic productivity (Archer and Mayer-Reimer, 1994; Sanyal et al., 1995). Phases of widespread breakdown in shallow-water carbonate production ("platform drowning") in Earth's history appear to coincide with phases of increased organic-carbon burial and with positive excursions in the $\partial^{13}C$ record (Lini et al., 1992; Föllmi et al., 1993, Föllmi et al., 1994). Also in such phases, eutrophication has played an important role in affecting the export ratio of organic carbon to carbonate carbon on a global scale, as is monitored by the $\partial^{13}C$ record (compare also Section 5.5.).

5.4. Natural temporal changes in the global phosphorus cycle

From the last Sections, it can be seen that variations in the global supply of phosphorus have important effects on ecology and the global carbon cycle. For a better understanding of such changes in the present and the geological past, a quantitative record of phosphorus burial through time on a global scale would be highly useful. Such a record would allow for a more precise modeling of phosphorus flux rates and a better assessment of the impact on productivity and the export ratio of organic carbon to carbonate carbon. Furthermore, a phosphorus burial record could be used as an approximation of temporal variations in the intensity of global continental weathering, which is the most important source of phosphorus (see Section 2.1.). Both productivity and continental weathering are, in turn, important sinks for atmospheric CO_2 (e.g., Raymo and Ruddiman, 1992), and a phosphorus burial record may, for this reason, display sensitivity towards paleoclimatologic variations on a time scale of several multiples of the oceanic residence time of phosphate (16–38 kyr; Ruttenberg, 1993).

A first, and widely used, quantification of phosphorite formation rates through Earth's history was published by Cook and McElhinny (1979; see also Cook, 1984 and Cook et al., 1990). This data set is based on an evaluation of estimated quantities of mined and minable sedimentary phosphorite deposits. These curves are, however, not necessarily proportional to the total amount of phosphate buried per time unit. They heavily depend on geological and economical aspects determining viability of a deposit, and may considerably change with the advent of new discoveries (Föllmi, 1993; Föllmi et al., 1993). A valid example is the mid-Cretaceous interval in this series, characterized by an apparent minimum in phosphorite formation. This minimum coincides with a maximum in hydrocarbon reservoir quantities (Klemme and Ulmishek, 1991), a relationship which has been used to support arguments for a general negative correlation of the phosphorus and carbon cycles (e.g., Arthur and Jenkyns, 1981). Phosphate-rich sediments of mid-Cretaceous age have been documented from many localities, especially from the Alpine–Himalayan mountain belt, Canada, Russia and the Pacific sea mounts, i.e., areas that are generally less intensively explored or poorly accessible (e.g., Fischer and Arthur, 1977; Ouwehand, 1987). However, with the recent discovery of lower Albian phosphate-rich sediments in the Blow River Formation of western Canada, the apparent minimum in mid-Cretaceous phosphorite formation may be transformed into a maximum (Yeo, 1990). Total P_2O_5 contents in this formation have been estimated as 7×10^9 tons, and this estimate alone qualifies the mid-Cretaceous as a period of considerable phosphorite formation, comparable in importance to the late Cretaceous and early Tertiary.

Compilations of vertical phosphorus distributions in sediment successions provide alternative, independent, phosphorus burial records. Here the crucial question is in how far the use of such time series can be expanded to a wider range of problems. An important difficulty is the observation that the amount and type of phosphate buried in sediments very much depend on local conditions such as the degree of bottom-water oxygenation, sediment-accumulation rate, water depth, sedimentation regime, amount of primary productivity and microbial activity on the sea floor and in the sediments. It turns out that these factors may influence phosphorus burial rates by several orders of magnitude on a regional scale (Baturin, 1982). This implies that, for a more representative reconstruction of phosphorus burial rates through time, a large number of sedimentary successions from different settings should be selected and compared in order to evaluate general trends in phosphorus burial.

An important compilation of phosphorus burial rates in marine sediments was presented by Cook (1984; based on Deep Sea Drilling Project Legs 22-28, i.e., Cretaceous and Tertiary sediments of the Indian Ocean; no correction for sediment compaction). With this series, he could show that the mid-Cretaceous was indeed a time of increased phosphate burial in the oceanic realm, at least for the Indian Ocean. The record by Cook (1984) shows trends in phosphorus burial which are comparable to the ones in the here presented compilation (compare also Föllmi et al., 1993). Detailed phosphorus time series for the Tertiary of the Pacific were published by Moody et al. (1988); compare also Moody et al. (1981), Zhou and Kyte (1992), Filippelli and Delaney (1992, Filippelli and Delaney (1994, Filippelli and Delaney (in press), Delaney and Filippelli (1994) and Filippelli et al. (1994). The compilations by G. Filippelli and M. Delaney are especially valuable because they used a sequential extraction method to determine the different phases in which phosphate was buried (compare Section 2.3). These

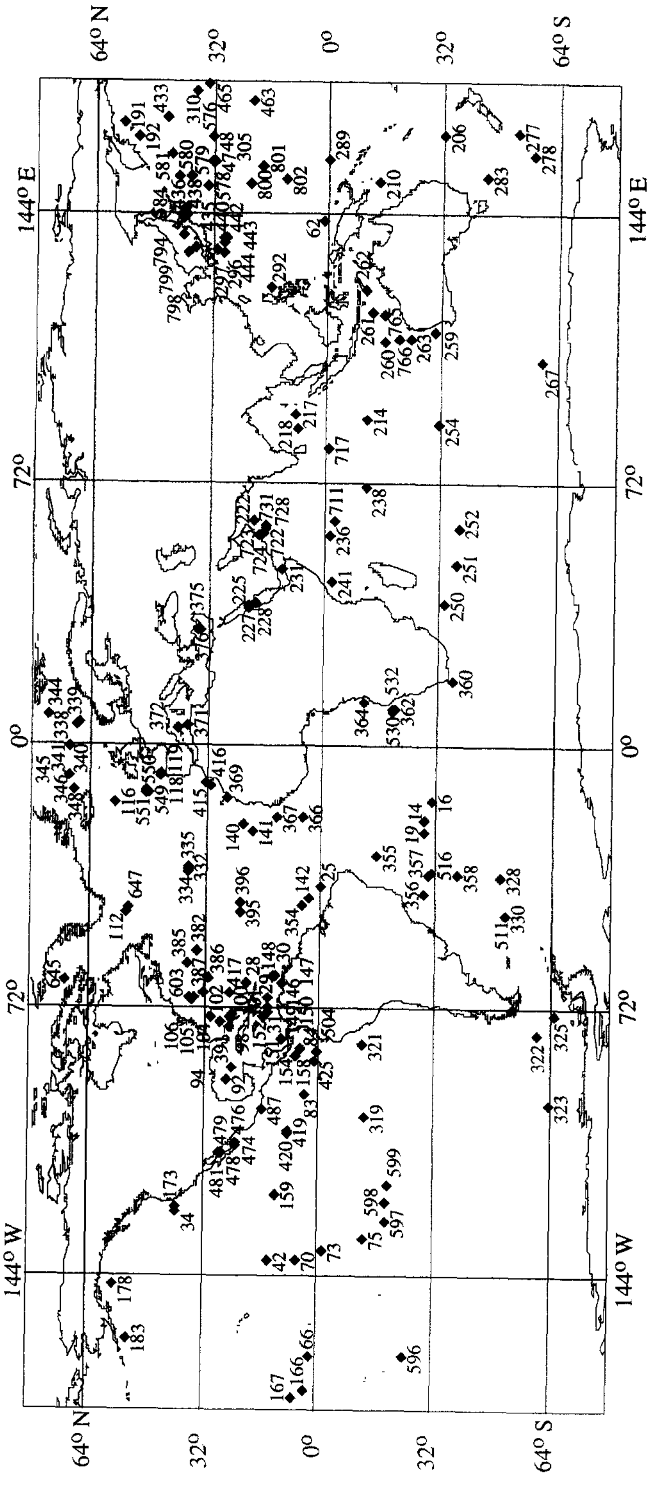


Fig. 17. World map showing locations of all Deep Sea Drilling Project and Ocean Drilling Program drill sites with published sedimentary phosphate contents, which have been used here. Table 2 gives additional information on the location of site, quantity of data, method used for phosphorus determination, and exact reference (from Föllmi, 1995a; reproduced with permission from the Geological Society of America).

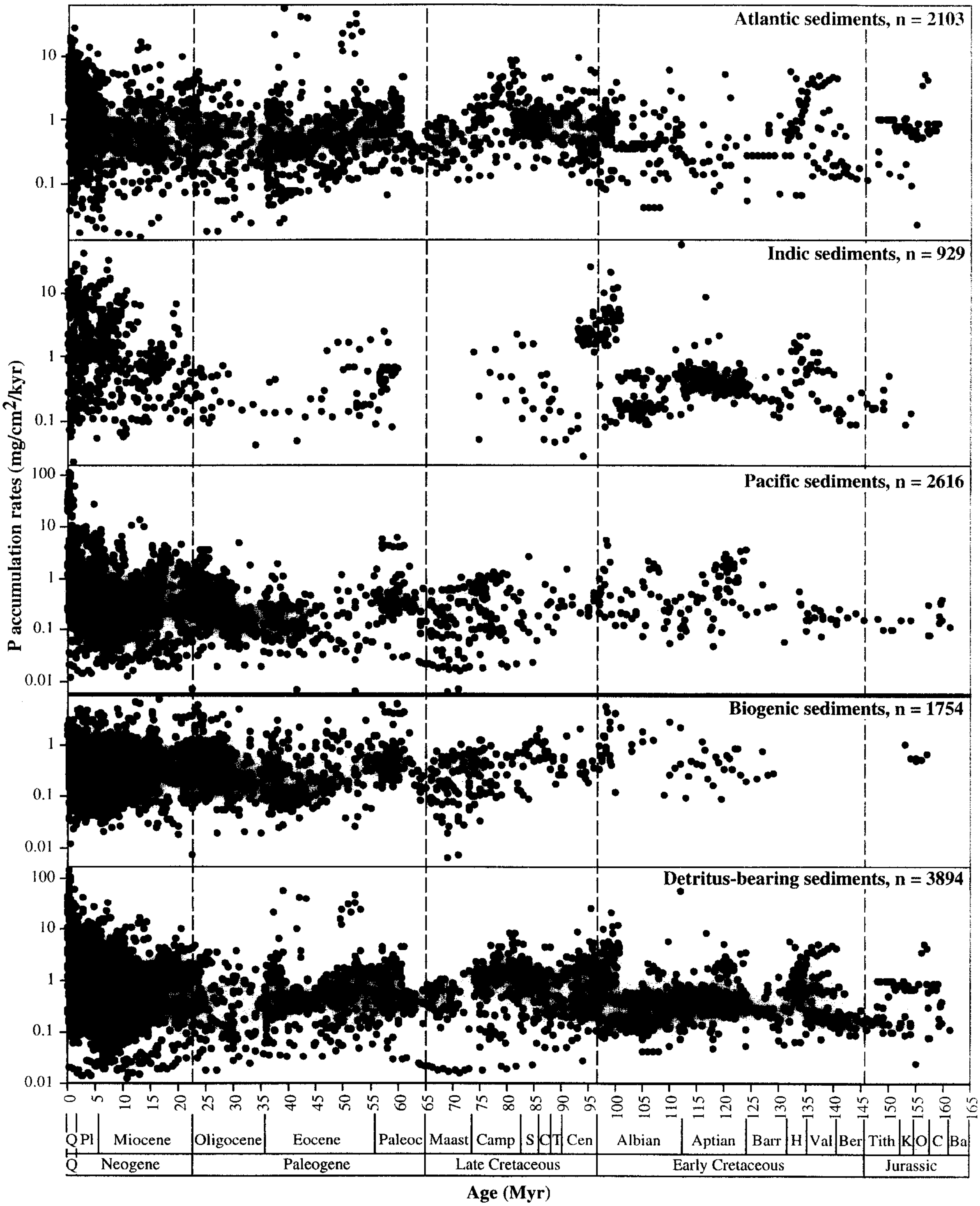


Fig. 18. Phosphorus accumulation rates for the past 160 Myr in sediments of the Atlantic, Indian and Pacific Oceans, as well as in biogenic sediments ($Al_2O_3 < 5\%$) and detritus-bearing sediments sediments ($Al_2O_3 > 5\%$). Data have been derived from Deep Sea Drilling Project and Ocean Drilling Program Legs 2-129.

phosphorus time series, however, are based on a restricted number of drill sites and onshore locations, and possibly include a strong regional component, which may be partly related to hydrothermal activity and phosphate-scavenging by iron minerals (e.g., Filippelli, 1994; Ruttenberg, 1994).

The phosphorus burial record discussed here is based on all phosphate data published in the proceedings of the Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP), to which a meaningful numerical age and sediment-accumulation rate can be assigned (Figs. 17–22; Table 2; Föllmi, 1995a). This last procedure is an essential part of the compilation and probably the major limiting factor in the quantification of this data set. The first problem arises with the choice

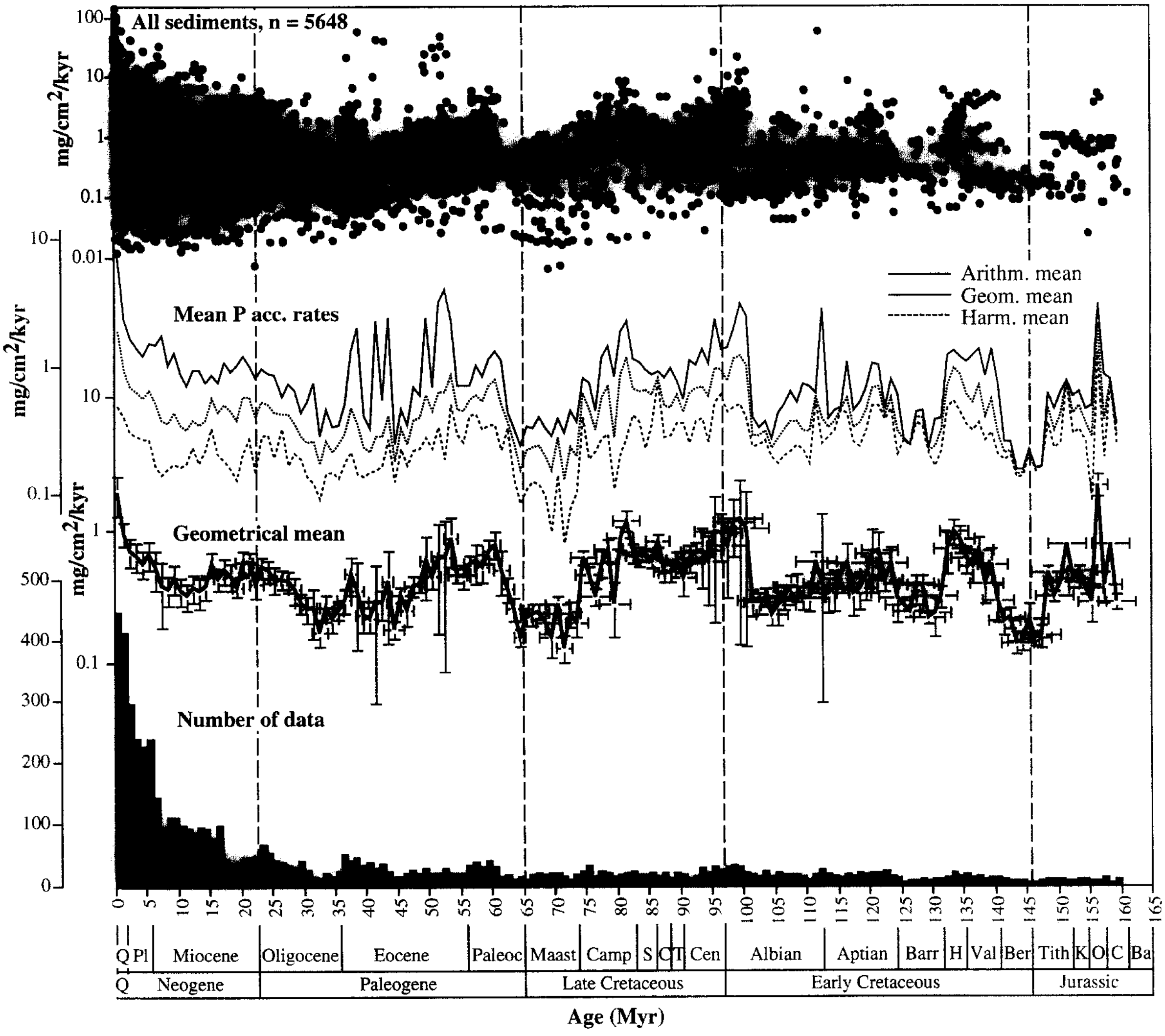


Fig. 19. Phosphorus accumulation rates for all areas and sediment types of Fig. 18. Arithmetical, geometrical, and harmonic means were calculated for each 1-Myr interval of this combined data base. Estimated error ranges are based on an estimation of the uncertainty in biostratigraphic dating and the corresponding uncertainty in sediment-accumulation rate (averaged in 1-Myr intervals) and are shown for the geometrical mean curve. Number of data used in each 1-Myr interval are shown at the base of the figure (modified after Föllmi, 1995a).

of the numerical time scale. Here, the time scale of Harland et al. (1990) is chosen, because it represents the most recent compilation that covers the entire time span investigated here (the past 160 Myr). The use of a more recent time scale for the younger part of the record would necessitate the combination of compilations from different authors, which would introduce additional uncertainty. Moreover, the detected phases of major change in phosphorus burial in the compilation presented here occur either within stages or are spread over more than one stage. This means that they are rather robust with regards to eventual changes in the numerical age length of a particular stage, which may occur when a new time scale is used. A second problem is the reliability of age determinations in the proceedings of DSDP and ODP (compare, e.g., Spencer-Cervato et al., 1994). Here, a conservative approach was taken with the assumption that determinations of guide fossils were correct. However, recent biostratigraphic distribution charts were employed in order to infer ages (in Bolli et al., 1989). The range of error in the phosphorus burial record was derived by estimating the possible error in age dating (generally up to 1 Myr for the Neogene, up to 2 Myr for the Paleogene and up to 3 Myr for the Cretaceous and late Jurassic), and the resulting error in calculated bulk sediment and phosphorus accumulation rates (Fig. 19

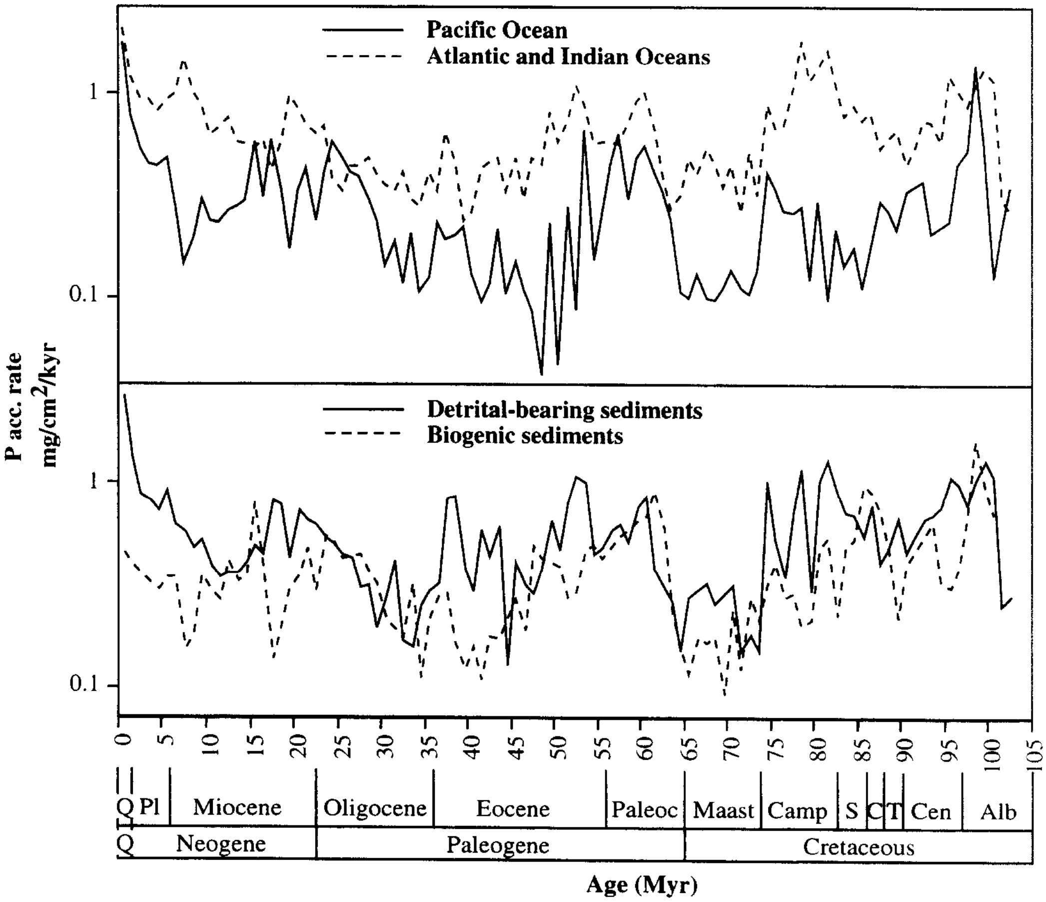


Fig. 20. Compilation of geometrical mean values of the records shown in Fig. 18 for the past 100 Myr. The incompleteness of the data set of the Indian Ocean does not allow for the reconstruction of a geometrical mean curve over longer time periods. This record was, for this reason, combined with that of the Atlantic Ocean.

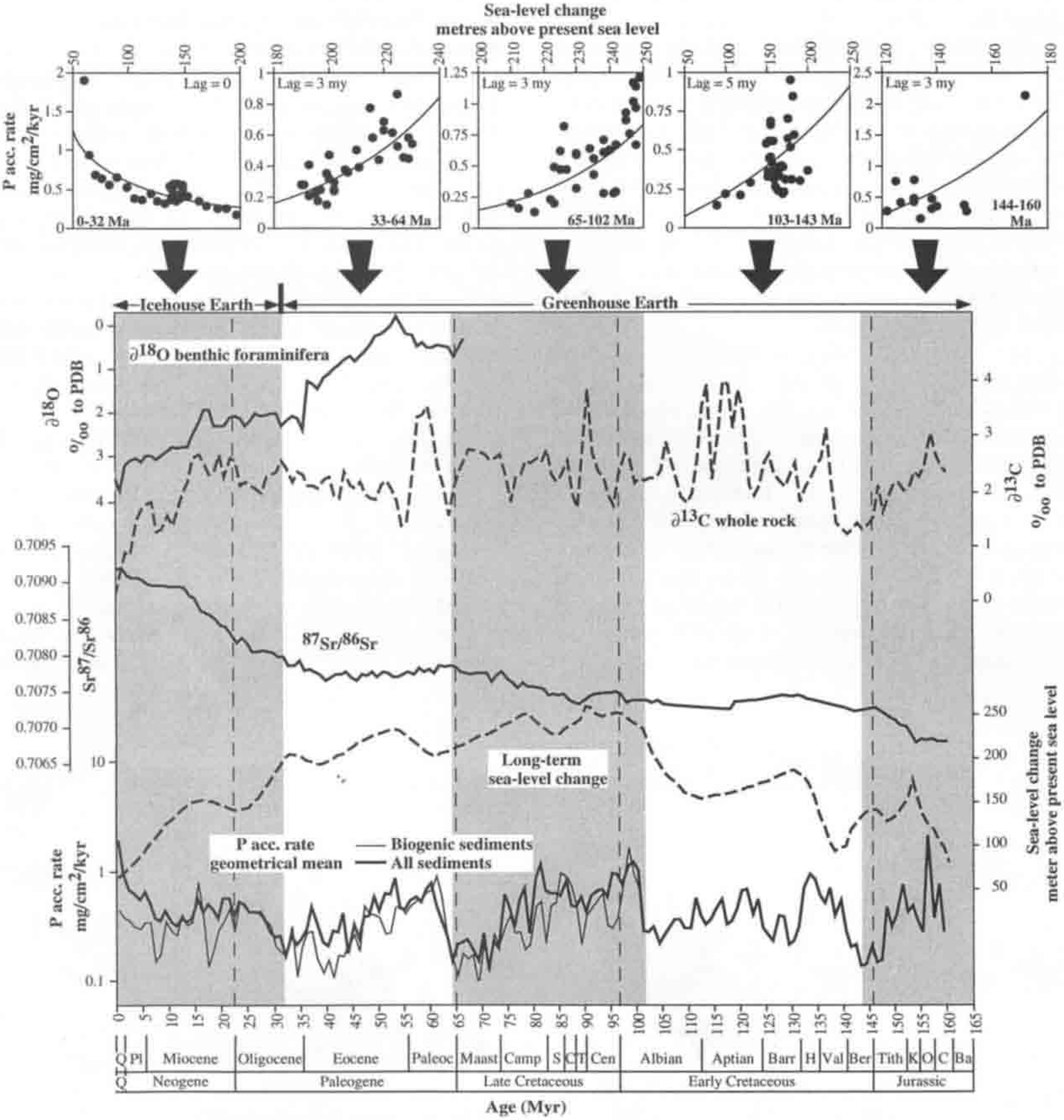


Fig. 21. Comparison of the total marine phosphorus accumulation curve from Fig. 19 and the biogenic marine phosphorus accumulation curve from Fig. 20 with other climate-sensitive curves. The episodes of rapid increase in phosphorus-burial rates followed by slow decrease in phosphorus-burial rates (i.e., Callovian–Berriasian, Berriasian–Albian, Albian–Paleocene, Paleocene–Oligocene) and the last episode of irregular increase in phosphorus-burial rates (Oligocene–present) are highlighted by alternating hatched and unhatched zones. Cross-correlation plots of sea level and total phosphorus burial are shown for each of these episodes. $\partial^{18}O$ adapted from Shackleton (1987), $\partial^{13}C$ from Renard (1986), Weissert and Lini (1991), Lini et al. (1992) and Bartolini et al. (1994), Föllmi et al. (1994), Jenkyns et al. (1994), long-term sea-level curve from Haq et al. (1987), and Sr^{87}/Sr^{86} from Jones et al. (1994) (modified from Föllmi, 1995a).

shows arithmetical means of all estimated errors in 1-Myr intervals).

Phosphorus accumulation rates (in mg/cm^2/kyr) were calculated by using linear sedimentation rates, dry bulk density (or wet bulk density, porosity, and water content), and phosphate contents. The phosphate contents were originally measured by colorimetric methods (molybdenum blue with stannous chloride) or X-ray fluorescence. Arthur et al. (1989) used both methods simultaneously on selected samples and showed that errors of reproducibility usually lie within 10% of the mean value.

The phosphorus burial record is composed of data subsets for the Atlantic, Indian and Pacific Oceans (Fig. 18). A further discrimination was made between biogenic sediments (sediments with < 5 wt.% Al_2O_3; i.e., pelagic nannofossil and foraminiferal sediments, diatomaceous sediments, and their diagenetic derivates, respectively) and detrital-bearing sediments (sediments with > 5 wt.% Al_2O_3; i.e., mostly shelf or slope sediments). The pelagic data subset is likely to lack a significant amount of detrital phosphate (but may include detrital eolian phosphate) and is used as an approximation for temporal variations in the availability of reactive, bioavailable, phosphate (Filippelli and Delaney, in press). The detritus-bearing data subset includes detrital phosphate, and can, as such, not be used as an approximation for variations in the bioavailability of phosphate alone. Geometrical mean values were calculated for these subdata sets (in 1-Myr intervals for the past 100 Myr; the records of the Indian Ocean were combined with those of the Atlantic, because of the presence of large hiatuses in the Indian Ocean record; Fig. 20), and arithmetical mean values, geometrical mean values, and harmonic mean values were compiled for the entire data set (also in 1-Myr intervals for the past 160 Myr; Fig. 19). The trends in the entire data base are traced quite comparably by these three different kinds of mean. The geometrical mean (corresponding to the *n*th root of the products of X_i: $GM = \sqrt[n]{\Pi X_i}$) was chosen as "standard" estimator because of its capability to deal with skewed data sets (Davis, 1986).

The database as a whole is characterized by considerable scatter, with phosphorus burial rates varying by two to four orders of magnitude. This

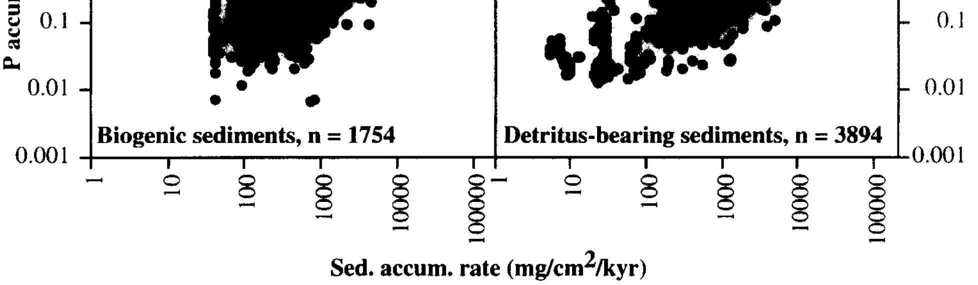


Fig. 22. Cross correlation plots of phosphorus accumulation rates and bulk sediment accumulation rates shown for the groups of biogenic sediments and detritus-bearing sediments (compare Fig. 18).

Table 2
List of Deep Sea Drilling Project and Ocean Drilling Program Sites with published phosphate data used in this study (see also Fig. 17). Abbreviations used: Type: D: Detrital-bearing sediments, B: Biogenic sediments; Age: Qu: Quaternary, Pl: Pliocene, Mi: Miocene, Ol: Oligocene, Eo: Eocene, Pa: Paleocene, Ma, Maastrichtian, Ca: Campanian, Sa: Santonian, Co: Coniacian, Tu: Turonian, Ce: Cenomanian, Al: Albian, Ap: Aptian, Ba: Barremian, Ha: Hauterivian, Va: Valanginian, Be: Berriasian, Ti: Tithonian, Ki: Kimmeridgian, Ox: Oxfordian, Cal: Callovian; References: IR: Initial Reports, SR: Scientific Results (from Föllmi, 1995a; reproduced with permission from the Geological Society of America).

Site	Lat.	Long.	Locality	Number of data	Type	Age	Leg	Method	References
9	32.8N	59.2W	Bermuda Rise	8	D	Qu-Mi	2	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
10	32.9N	52.2W	Mid-Atlant. Ridge	10	D	Pl-Eo			
14	28.3S	20.9W	Mid-Atlant. Ridge	11	B	Qu-Mi	3	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
16	30.3S	15.7W	Mid-Atlant. Ridge	15	B	Qu-Mi			
19	28.5S	23.7W	Mid-Atlant. Ridge	16	B	Ol-Eo			
25	0.5S	39.2W	NE Brazil	16	B	Qu-Mi	4	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
28	20.6N	65.6W	Puerto Rico Tr.	2	D	Eo			
29	14.8N	69.3W	Venezuelan Basin	40	D	Qu-Eo			
30	12.9N	63.4W	Aves Ridge	17	D	Qu-Mi			
31	14.9N	72W	Beata Rise	17	B	Qu-Ol			
34	39.5N	127.3W	Delgada Fan	44	D	Qu-Mi	5	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
42	13.8N	140.2W	Clarion Fract. Z.	31	B	Ol-Eo			
44	19.3N	169W	Horizon Ridge	20	B	Ol-Eo	6	Colorimetry	Lisitzin, 1971, DSDP, IR, 6, 829
47	32.4N	157.7E	Shatsky Plateau	21	B	Pl-Ma			
48	32.4N	158E	Shatsky Plateau	3	B	Ma			
62	1.9N	141.9E	Eauripik Ridge	25	B	Qu-Mi	7	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
66	2.4N	166.1W	C. Pacific Basin	22	B	Qu-Ol			
70	6.3N	140.4W	Clipperton Fr. Z.	41	B	Qu-Eo	8	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
73	1.9S	137.5W	C. equat. Pacific	27	B	Qu-Eo			
75	12.5S	134.3W	SE Marquesas Isl.	22	B	Mi-Ol			
83	4N	95.7W	East Pacific Rise	19	B	Qu-Mi	9	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
84	5.7N	82.9W	East Pacific	25	D	Qu-Mi			
92	25.8N	91.8W	Gulf of Mexico	13	D	Qu-Pl	10	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
94	24.5N	88.5W	Yucatan Shelf	31	B	Qu-Pa			
98	25.4N	77.3W	Bahama's	17	B	Qu-Pa	11	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
100	24.7N	73.8W	Bahama's	3	B	Ox-Cal			
101	25.2N	74.4W	Blake-Bahama's	9	D	Al-Va			
102	30.7N	74.5W	Blake-Bahama's	23	D	Qu-Mi			
104	30.8N	74.3W	Blake-Bahama's	15	D	Mi			
105	34.9N	69.2W	SE New York	52	D	Qu-Ox			
106	36.4N	69.5W	SE New York	12	D	Qu-Mi			
112	54N	46.6W	S Labrador Sea	21	D	Qu-Eo	12	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
116	57.5N	15.9W	Hatton-Rockall B.	30	B	Qu-Eo			
118	45N	9W	Bay of Biscay	12	D	Qu-Pl			
119	45N	8W	Bay of Biscay	32	D	Qu-Pa			
140	21.7N	21.8W	W Cape Blanc	14	D	Pl-Ma	14	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
141	19.4N	24W	N Cape Verde Isl.	13	B	Qu-Mi			
142	3.4N	42.4W	Ceara Abyss. Pl.	27	D	Qu-Mi			
146	15.1N	69.4W	Venezuelan Basin	27	B	Mi-Co	15	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
147	10.7N	65.2W	Cariaco Basin	22	D	Qu			
148	13.4N	63.7W	Aves Ridge	27	D	Qu-Pl			
149	15.1N	69.4W	Venezuelan Basin	34	B	Qu-Eo			
150	14.5N	69.4W	Venezuelan Basin	3	D	Mi			
151	15N	73.4W	Caribbean Sea	16	B	Qu-Pa			
152	15.9N	74.6W	Nigaragua Rise	22	B	Eo-Ca			
154	11.1N	80.4W	Colombian Basin	17	D	Qu-Pl			
158	6.6N	85.2W	Cocos Ridge	29	B	Qu-Mi	16	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
159	12.3N	122.3W	East Pacific Rise	25	D	Qu-Ol			
166	3.8N	175.1W	C. Pacific Basin	28	B	Pl-Eo	17	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
167	7.1N	176.8W	C. Pacific Basin	28	B	Qu-Eo			
173	40N	125.5W	S Mendocino R.	16	B/D	Qu-Mi	18	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
178	57N	147.1W	Alaskan Ab. Plain	26	D	Qu-Mi			
183	52.6N	161.2W	Aleutian Ab. Plain	36	D	Qu-Mi	19	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
191	56.9N	168.2E	Kamchatka Basin	10	D	Qu-Pl			
192	53N	164.7E	Meiji Guyot	54	D	Qu-Ma			
206	32S	165.5E	New Caledonia B.	39	B	Qu-Pa	21	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
210	13.8S	152.9E	Coral Sea Basin	21	D	Qu-Eo			
213	10.2S	93.9E	NW Cocos Island	16	D	Qu-Pa	22	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
214	11.3S	88.7E	Ninetyeast Ridge	22	B	Qu-Eo			
217	8.9N	90.5E	Ninetyeast Ridge	22	B	Qu-Pa			
218	8N	86.3E	C Bengal Fan	30	D	Qu-Mi			
222	20.1N	61.5E	Off Arabia	29	D	Qu-Mi	23	???	Manheim, 1974, DSDP, IR, 23, 923
225	21.3N	38.3E	Red Sea	6	D	Qu-Pl		Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
227	21.3N	38.1E	Red Sea	6	D	Qu-Pl			

Table 2 (continued)

228	19.1N	39E	Red Sea	5	D	Qu-Pl			
231	11.9N	48.2E	Off Somalia	25	B	Qu-Mi	24	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
236	1.7S	57.6E	N Seychelles Isl.	29	B	Qu-Pa			
238	11.2S	70.5E	Chagos Archipel.	12	B	Qu-Ol			
241	2.4S	44.7E	East African c. r.	26	D	Qu-Sa	25	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
250	33.5S	39.4E	Mozambique Basin	25	D	Qu-Co	26	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
251	36.5S	49.5E	SW Indian Ridge	10	B	Qu-Mi			
252	37S	59.2E	Crozet Basin	6	D	Mi			
254	31S	87.9E	S Ninetyeast R.	17	B	Qu-Ol			
259	29.6S	112.7E	Perth Abyss. Pl.	125	D	Qu-Ap	27	Colorimetry	Cook, 1974, DSDP, IR, 27, 455
260	16.1S	110.3E	Gascoyne Ab. Pl.	13	D	Al			
261	12.9S	117.9E	Argo Abys. Plain	65	D	Qu-Ki			
262	10.9S	123.8E	Timor Trough	29	D	Qu-Pl			
263	23.3S	111E	Cuvier Abys. Pl.	64	D	Qu-Al			
266	56.3S	110.1E	SE Indian Ridge	23	B	Qu-Mi	28	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
267	59.3S	104.5E	SE Indian Ridge	7	D	Mi			
277	52.2S	166.2E	Campbell Plateau	11	B	Qu-Pa	29	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
278	56.6S	160.1E	S Emerald Basin	26	B	Qu-Mi			
283	43.9S	154.3E	C. Tasman Sea	15	D	Eo-Pa			
289	0.5S	158.5E	E Solomon Islands	44	B	Qu-Ap	30	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
292	15.8N	124.7E	Benham Rise	39	B	Qu-Eo	31	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
296	29.3N	133.5E	Off Kyushu	20	D	Qu-Mi			
297	30.9N	134.2E	Off Kyushu	18	D	Qu-Mi			
305	32N	157.9E	Shatsky Rise	36	B	Qu-Ca	32	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
310	36.9N	176.9E	Hess Rise	31	B	Qu-Sa			
319	13S	101.5W	Bauer Deep	23	B	Pl-Mi	34	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
321	12S	81.9W	Peru Basin	46	B/D	Qu-Eo			
322	60S	79.4W	Bellinghausen A.P.	11	D	Pl-Mi	35	Colorimetry	Donelly, 1976, DSDP, IR, 35, 427
323	63.7S	98W	Bellinghausen A.P.	53	D	Pl-Ma		Colorimetry	Bogdanov, 1976, DSDP, IR, 35, 447
325	65S	73.7W	Antarctic cont. r.	35	D	Pl-Mi			
328	49.8S	36.7W	Malvinas Outer B.	27	D	Qu-Sa	36	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
330	50.9S	46.9W	Falkland Plateau	3	D	Ox			
332	36.9N	33.6W	Mid-Atlant. Ridge	4	B	Qu-Pl	37	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
333	36.9N	40W	Mid-Atlant. Ridge	4	B	Qu-Pl			
334	37N	34.4W	Mid-Atlant. Ridge	4	B	Qu-Mi			
335	37.3N	35.2W	Mid-Atlant. Ridge	6	B	Pl-Mi			
338	67.8N	5.4E	Vøring Plateau	24	D	Qu-Eo	38	XRF	Nesterova, 1978, DSDP, IR, 38S, 73
339	67.2N	6.3E	Vøring Plateau	23	B/D	Qu-Ol		???	Emelyanov, 1978, DSDP, IR, 38S, 31
340	67.2N	6.3E	Vøring Plateau	33	B	Eo		???	Kossovskaya, 1978, DSDP, IR, 38S, 45
341	67.3N	6.1E	Vøring Plateau	22	D	Qu-Mi		Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
344	76.1N	7.9E	Knipovich Ridge	14	D	Qu-Pl			
345	69.8N	1.2W	Lofoten Basin	10	D	Ol-Eo			
346	69.9N	8.7W	Jan Mayen Ridge	14	D	Qu-Mi			
348	68.5N	12.5W	Islandic Plateau	63	D	Qu-Ol			
354	5.9N	44.2W	Ceara Rise	41	B	Qu-Ma	39	Colorimetry	Emelyanov, 1977, DSDP, IR, 39, 477
355	15.7S	30.6W	Brazil Basin	26	B/D	Mi-Ca		Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
356	28.3S	41.1W	Sao Paulo Plateau	29	D	Pl-Tu			
357	30S	35.6W	Rio Grande Rise	64	B	Pl-Co			
358	37.7S	36W	Argentine Basin	44	D	Qu-Ma			
360	35.8S	18.1E	Cape Basin	18	B	Pl-Eo	40	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
362	19.8S	10.5E	Walvis Ridge	20	B	Qu-Eo			
364	11.6S	12E	Angola c. marg.	18	B/D	Qu-Al			
366	5.7N	19.9W	Sierra Leone Rise	36	B	Qu-Pa	41	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
367	12.5N	20W	Cape Verde Basin	3	B	Ki-Ox			
369	26.6N	15W	Off Cape Bojador	15	B	Mi-Al			
371	37.6N	5.3E	S Balearic Basin	8	D	Qu-Pl	42	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
372	40.1N	4.8E	Menorca Rise	26	D	Qu-Mi			
375	34.8N	31.8E	Florence Rise	13	D	Mi			
376	34.9N	31.8E	Florence Rise	14	D	Qu-Mi			
382	34.4N	56.5W	Nashville Seam.	26	D	Qu-Ca	43	XRF	Murdmaa, 1979, DSDP, IR, 43, 675
385	37.4N	60.2W	Vogel Seamount	2	D	Ol-Ma		Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
386	31.2N	64.2W	C. Bermuda Rise	61	D	Ol-Al			
387	32.3N	67.7W	W Bermuda Rise	37	D	Qu-Be			
391	28.2N	75.6W	Blake-Bahama's	11	D	Al-Va	44	Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
395	22.8N	46.1W	Mid-Atlant. Ridge	23	D	Qu-Pl	45	Spectral Anal.	Timofeev, 1979, DSDP, IR, 45, 323
396	22.5N	43.5W	Mid-Atlant. Ridge	40	D	Qu-Pl			
415	31N	11.7W	Agadir Canyon	23	D	Qu-Al	50	Colorimetry	Migdisov, 1980, DSDP, IR, 50, 675

Table 2 (continued)

416	32.8N	10.8W	Moroccan Basin	22	D	Mi-Ti			
417	25.1N	68W	S Bermuda Rise	33	D	Qu-Ap	51-53	Colorimetry	Donelly, 1980, DSDP, IR, 51-53, 1515
418	25N	68W	S Bermuda Rise	6	D	Al			
419	8.9N	105.7W	East Pacific Rise	4	B	Qu	54	XRF	Schrader, 1980, DSDP, IR, 54, 319
420	9N	106.1W	East Pacific Rise	27	B	Qu-Pl		Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
425	1.4N	86.1W	East Pacific Rise	8	B	Qu			
433	44.8N	170E	Suiko Seamount	10	B	Mi-Pa	55	XRF	Murdmaa, 1980, DSDP, IR, 55, 457
								Colorimetry	Donelly, 1980, DSDP, IR, 54, 899
435	39.7N	143.8E	Japan Trench	22	D	Qu-Pl	56-57	XRF	Sugisaki, 1980, DSDP, IR, 56-57, 1233
436	39.9N	145.6E	Japan Trench	64	D	Qu-Mi			
438	40.6N	143.2E	Japan D.S. Ter.	48	D	Qu-Mi			
440	39.7N	143.9E	Japan Trench	37	D	Qu-Mi			
442	29N	136.1E	Shikoku Basin	57	D	Qu-Mi	58	XRF	Sugisaki, 1980, DSDP, IR, 58, 719
443	29.3N	137.4E	Shikoku Basin	77	D	Qu-Mi			
444	28.6N	137.7E	Shikoku Basin	72	D	Qu-Mi			
463	21.4N	174.7E	Mid-Pacific M.	58	B	Qu-Ba	62	Wet chemical	Varentsov, 1981, DSDP, IR, 62, 785
465	33.8N	178.9E	S Hess Rise	22	B	Pa-Al			
474	23N	109W	Baja California	11	D	Qu-Pl	64	XRF	Niemitz, 1982, DSDP, IR, 64, 695
476	23N	109.1W	Baja California	6	D	Qu-Pl			
478	27.1N	111.5W	Guaymas Basin	16	D	Qu			
479	27.8N	111.6W	Guaymas Basin	14	D	Qu-Pl			
481	27.3N	111.5W	Guaymas Basin	12	D	Qu			
487	15.9N	99.2W	Pacific n. Mexico	42	D	Qu-Mi	66	ICPMS	Leggett, 1982, DSDP, IR, 66, 683
504	1.2N	83.7W	S Costa Rica Drift	33	B	Qu-Mi	69	XRF	Beiersdorf, 1983, DSDP, IR, 69, 343
511	51S	47W	Falkland Plateau	113	D	Ca-Cal	71	Emission Sp.	Varentsov, 1983, DSDP, IR, 71, 391
516	30.3S	35.3W	Rio Grande Rise	23	B	Pl-Ca	72	XRF	Emelyanov, 1983, DSDP, IR, 72, 421
530	19.2S	9.4E	Angola Basin	192	D	Pl-Al	75	XRF	Dean, 1984, DSDP, IR, 75, 923
532	19.7S	10.5E	Walvis Ridge	48	D	Qu-Mi			
549	49.1N	13.1W	Goban Spur	5	D	Ce-Ha	80	Pl.Opt.Em.Sp.	Cunningham, 1985, DSDP, IR, 80, 1073
550	48.5N	13.4W	Goban Spur	25	B	Pl-Al			
551	48.9N	13.5W	Goban Spur	5	B	Ca-Ce			
576	32.4N	164.3E	Emperor- Shatsky	149	D	Qu-Ca	86	XRF	Heath, 1985, DSDP, IR, 86, 605 & 657
578	33.9N	151.6E	Shatsky Rise	76	D	Qu-Mi			
579	38.6N	153.8E	Kuril-Shatsky	46	D	Qu-Pl			
580	41.6N	154E	Kuril-Shatsky	33	D	Qu-Pl			
581	43.9N	159.8E	Kuril-Emperor	60	D	Pl-Mi			
584	40.5N	144E	Japan Trench	18	D	Pl-Mi	87	XRF	Minai, 1986, DSDP, IR, 87, 643
596	23.9S	165.7W	S Pacific	64	D	Qu-Sa	91	XRF	Zhou, 1992, Paleoceanography, 7, 441
597	18.8S	129.8W	Mendoza Rise	32	B	Mi-Ol	92	XRF	Lyle, 1986, DSDP, IR, 92, 355
598	19S	124.7W	East Pacific Rise	135	B	Qu-Mi			
599	19.5S	119.9W	East Pacific Rise	39	B	Pl-Mi			
603	35.5N	70W	N American Basin	55	D	Eo-Va	93	XRF	Dean, 1987, DSDP, IR, 93, 1093
645	70.46N	64.65W	Baffin Bay	10	D	Mi	105	Emission Sp.	Thiébault, 1989, ODP, SR, 105, 83
647	53.33N	45.26W	S Labrador Sea	112	D	Ol-Eo		XRF, ICPMS	Arthur, 1989, ODP, SR, 105, 111
								Spectroph.	Bohrmann, 1989, ODP, SR, 105, 137
711	2.74S	61.16E	W eq. Indian Oc.	22	D	Qu-Mi	115	ICPAES	Boström, 1990, ODP, SR, 115, 699
717	0.93S	81.39E	Bengal Fan	75	D	Qu-Mi	116	XRF	Shipb. P., 1988, ODP, IR, 116, 45
								XRF	Crowley, 1990, ODP, SR, 116, MFiche
722	16.62N	59.8E	Owen Ridge	4	B	Qu	117	XRF	Shimmield, 1991, ODP, SR, 117, 409
723	18.05N	57.61E	Off Saudi Arabia	7	D	Qu-Pl		XRF	Jarrard, 1991, ODP, SR, 117, 473
724	18.46N	57.79E	Off Saudi Arabia	9	D	Qu			
728	17.68N	57.83E	Off Saudi Arabia	5	D	Pl-Mi			
731	16.47N	59.7E	Owen Rdige	24	D	Mi			
765	15.98S	117.58E	Argo Abys. Plain	137	D	Qu-Ti	123	XRF	Shipb. P., 1990, ODP, IR, 123, 63
766	19.93S	110.45E	Gascoyne Ab. Pl.	20	D	Tu-Va		XRF	Plank, 1992, ODP, SR, 123, 167
								XRF	Heggie, 1992, ODP, SR, 123, 225
794	40.19N	138.23E	Yamato Basin	70	D	Qu-Mi	128	XRF	Shipb. P., 1990, ODP, IR, 128, 237
798	37.04N	134.8E	Oki Ridge	15	D	Qu-Pl		XRF + Aspilla	Föllmi, 1992, ODP, SR, 127-128, 63
799	39.22N	133.87E	Kita-Yamato Tr.	12	D	Qu-Mi		XRF	Föllmi, 1992, ODP, SR, 127-128, 559
								XRF	Tada, 1992, ODP, SR, 127-128, 1229
800	21.92N	152.32E	Pigafetta Basin	74	D	Ca-Va	129	Spectrometry	Karpoff, 1992, ODP, SR, 129, 3
801	18.64N	156.36E	Pigafetta Basin	56	D	Pa-Cal		XRF	Karl, 1992, ODP, SR, 129, 31
802	12.1N	153.21E	Mariana Basin	9	D	Eo-Al			

scatter masks general trends in a considerable manner and the search for such trends can only be done if the subdata sets are considered independently (Fig. 20). A comparison of the combined Atlantic–Indian Ocean record with the Pacific record suggests that the general, first-order trends are comparable but that considerable differences exist on a shorter time scale (especially in the Oligocene and Miocene). In both records, phosphorus burial rates increased in the late Albian, decreased during the early late Cretaceous and increased in the Turonian, respectively the Coniacian to a maximum in the Campanian (with a lag between both records). In both records, the Maastrichtian is characterized by a minimum and the Paleocene by a first-order increase. In the Eocene, an irregular decrease was followed by an increase in both records. From the Oligocene onwards, both records show an irregular and poorly comparable increase in phosphorus burial rates, a trend which continued until today. A major difference in both records is the late Miocene interval, which, in the Pacific, is characterized by a relative minimum, whereas, in the Atlantic–Indian Ocean realm, a relative maximum existed. A comparison of phosphorus burial rates in biogenic and detritus-bearing sediments points to a good general correlation, with major departures only in the late Eocene and early Miocene. The same is true for the correlation between the burial curves in biogenic sediments and all sediments (Fig. 21). The differences in the Atlantic–Indian Ocean curve and the Pacific curve may be related to ocean-to-ocean fractionation effects (on a time scale of several Myr), which could be due to highly unequal rates of phosphorus supply in both realms. For instance, in the Oligocene and Neogene, glaciation processes and increased erosion rates in newly formed mountain areas (alpine mountain belt, the Himalaya area) may have led to a greatly enhanced phosphorus supply into the Indian and Atlantic Oceans, relative to the Pacific (compare Raymo, 1994). The similarity in the long-term trends in all subdata sets suggests that the entire dataset has a certain robustness. This encouraged me to take the geometrical mean curve of the entire data set as an approximation of global marine sedimentary phosphorus accumulation rates, bearing in mind that shorter-term intra-oceanic fractionation processes may considerably alter this record for each individual ocean.

The geometrical mean record of phosphorus burial for all sediments shows variations of around one order of magnitude or less. Times of significant increase in phosphorus burial occurred in the Callovian–Oxfordian, Valanginian–Hauterivian, late Albian and Paleocene. These rather short periods (3–10 Myr) were followed by longer periods (15–35 Myr) of gradual and irregular decrease in marine phosphorus burial rates (Figs. 19 and 21). Noticeable periods of relative high phosphorus accumulation rates were the Albian to Campanian, the Paleocene–early Eocene, the Oligocene–early Miocene and the Plio-Pleistocene. Of interest is the close correlation between the total and biogenic phosphorus burial curves (Fig. 21), which suggests that changes in total phosphorus burial were closely matched by changes in burial rates of reactive, bioavailable, phosphate. This hints at the possibility that changes in total rates of continental weathering (as the prime source of phosphate) are paralleled by changes in rates of biochemical continental weathering rates (as the main long-term source of reactive phosphate).

When compared to the carbonate $\partial^{13}C$ curve (Fig. 21), we see a reasonably good correlation between times of major increase in marine phosphorus burial rates and periods of 1-2-‰ positive excursions in the $\partial^{13}C$ curve (an exception is the late Albian, where the corresponding $\partial^{13}C$ excursion is comparatively small). Note that the positive $\partial^{13}C$ excursion at the Cenomanian–Turonian boundary is not imaged by the marine phosphorus burial curve. The rates and changes during the long periods of general decline in phosphorus burial are rather poorly correlated to the $\partial^{13}C$ record. This may suggest that, in general, times of increased phosphorus burial, i.e., times of widespread eutrophication, may indeed have affected the export ratio of organic carbon to carbonate carbon on a global scale, thereby causing a positive excursion in $\partial^{13}C$ values (see Sections 5.3. and 5.5.). Some positive $\partial^{13}C$ excursions, however, appear not to be explainable by the effect of eutrophication episodes alone and other environmental factors need to be considered as well. This finding suggests that the conclusions of Föllmi et al. (1994), who associated early Cretaceous positive $\partial^{13}C$ excursions with eutrophic events, cannot be extrapolated to $\partial^{13}C$ excursions in general, but that each $\partial^{13}C$ event needs to be considered in its own environmental context.

The correlation between the $^{87}Sr/^{86}Sr$ curve with the phosphorus burial curve is of interest, because the $^{87}Sr/^{86}Sr$ curve is used as an independent indicator of uplift rates and continental weathering (e.g., Berner, 1994, who listed possible pitfalls in the use of this parameter). In general, correlation between these two time series is rather poor (Fig. 21). Phases of rapid increase in marine phosphorus burial rates in the Callovian–Oxfordian, late Albian and Paleocene appear to correspond to relatively flat or even negative $^{87}Sr/^{86}Sr$ trends, whereas times of decrease in phosphorus burial in the late Jurassic, late Cretaceous and middle to late Miocene correspond to positive trends in the $^{87}Sr/^{86}Sr$ record. However, these correlations cannot be extrapolated to the entire length of both records. This suggests that caution is needed in an eventual linking of these records.

A peculiar correlation is seen between phosphorus burial and long-term sea-level change (and also the $\partial^{18}O$ record in benthic foraminifera; Fig. 21). Prior to approximately 32 Ma, this correlation appears to be positive but phase-shifted by several Myr (compare cross-correlation plots in Fig. 21; note that the sea-level record for the Albian is poorly constrained and that new results suggest a major sea-level rise in the latest Albian; e.g., Grötsch et al., 1993). From approximately 32 Ma to the present, an inverse correlation is observed (substantiated by cross correlation; Fig. 21). Interpretation of these covariations can only be preliminary and further research is warranted, specifically with a focus on the time windows of major change. Prior to 32 Ma, the positive, albeit phase-shifted, correlation between long-term sea-level rise and increases in the phosphorus burial record suggests that times of increased phosphorus flux rates occurred during transgressive phases, a juxtaposition that has been observed by many authors (e.g., Arthur and Jenkyns, 1981; compare also Section 4.3.). The periods of rapid increase in global marine phosphorus burial rates in the Callovian–Oxfordian, Valanginian–Hauterivian, late Albian and Paleocene are viewed as periods of rapid global warming, in which continental weathering rates became globally enhanced. This is probably due to the combined effect of the spreading of warm and humid tropical climate belts and tectonic reorganizational processes, which were often coupled with major flood-basalt formation (e.g., Rea et al., 1990; Larson, 1991; Caldeira and Rampino, 1991; Jones et al., 1994). The lag time between sea-level change and phosphorus burial could be related to the possibility that periods of tectonic reorganization led to the immediate release of substantial amounts of greenhouse-active gases (mainly primordial CO_2; e.g., Schlanger et al., 1981; Arthur et al., 1985; Rea et al., 1990; Caldeira and Rampino, 1991), whereas several million years were needed to produce sufficient young and hot oceanic crust and/or submarine plateau basalts to force sea level to rise.

The inverse correlation between phosphorus burial and sea level in the time from 32 Ma to the present suggests that a new mechanism responsible for the acceleration of the phosphorus cycle came into play, a mechanism that is different from the ones prior to 32 Ma and powerful enough to overrule these previous mechanisms. One possible mechanism is intensified orogeny and relief formation. This mechanism may indeed be important, but two arguments are used here to show that it was not the major triggerer of the flip in feedback between weathering mechanisms and environment at around 32 Ma: (1) there is no obvious dependency between relief formation and sea-level change, whereas the mechanism to be identified here is correlated to sea-level change; (2) phases of uplift and relief formation in the Himalayan area (as a prime target of weathering during the Oligocene and Neogene) does not seem to correspond to phases of accelerated phosphorus burial. A major phase of uplift and relief formation in the Himalayan area has been identified in the period of 21–17 Ma (Raymo, 1994, compare also Searle, 1995, and Coleman and Hodges, 1995). This phase is not reflected in the phosphorus burial curve discussed here. On the other hand, the large increase in phosphorus burial observed in the last 7 Myr does not appear to correlate to a phase of increased uplift and relief formation (Molnar and England, 1990).

The mechanism that is probably instrumental in driving weathering rates from the Oligocene onward is glaciation (Föllmi, 1995a; compare also Zachos et al., 1994). Glacial erosion is known to be very effective in grinding solid bedrock (rates of 1–20 mm/yr; e.g., White et al., 1992). Moreover, an important observation is that chemical erosion rates can be significantly enhanced in glacial environments (Sharp et al., 1995), which is probably related to the production of high amounts of reactive mineral surface. The massive appearance of continental glaciers and ice sheets in the early Oligocene (e.g., Zachos et al., 1992) transformed the mode of coupling of global warming, increased weathering, and increased phosphorus supply ("greenhouse earth mode"; Fig. 21) into a mode coupling global cooling, increased glacial erosion, and increased phosphorus supply ("icehouse earth mode"; Fig. 21).

The correlation between long-term sea-level fall and increased phosphorus burial in the last 32 Myr does not exclude the possibility that short-term maxima in phosphorus burial and phosphogenesis coincided with short-term sea-level rise superimposed on the long-term trend of sea-level fall. For instance, the episode of phosphogenesis in the late early–early middle Miocene appears to have coincided with a period of warming superposed on a long-term cooling trend (e.g., Compton et al., 1990, Compton et al., 1993). Another important result was obtained by Hiatt (1994), who found that periods of major phosphogenesis within the Permian Phosphoria Formation, which apparently formed during an interval of major glaciation, coincided with periods of relative sea-level fall. The Permian may, therefore, be comparable to the present-day in terms of glaciation being a major factor controlling continental weathering rates.

Cross-correlation diagrams (Fig. 22) show a positive correlation between phosphorus accumulation rates and overall sediment accumulation rates, both for the biogenic sediment subdata set, as well as for the detritus-bearing sediment subdata set. These diagrams show a dependency between the amount of delivered (detrital) and biogenically produced sediments and phosphate flux rates. This relationship underscores the importance of the phosphorus burial curve as an indicator of continental weathering and oceanic productivity.

In general, time series of marine phosphorus burial may help to delineate mechanisms of climate change and clear up equivocal relationships between global weathering and climate (e.g., François et al., 1993). Furthermore, they may also help to clarify relationships between climate and primary productivity. Several uncertainties related to global phosphorus burial should, however, be pointed out: Ingall et al. (1993, Ingall et al. (1994), Ingall and Jahnke (1994) and Van Cappellen and Ingall (1994) suggested that during times of widespread oceanic anoxia, overall phosphorus burial rates may be substantially lowered because of the decreased capacity of sediments to hold back phosphate. The phosphorus burial curve show generally high levels of phosphorus burial for periods which are inferred to have been "anoxic" (e.g., Valanginian, Aptian, Cenomanian–Turonian boundary and Santonian; e.g., Schlanger and Jenkyns, 1976; Arthur and Schlanger, 1979; Lini et al., 1992). An exact correlation of the "oceanic anoxic events" with the phosphorus burial curve reveals that the early and early late Aptian and the Cenomanian–Turonian boundary "anoxic events" may coincide with brief periods of decrease in marine phosphorus burial rates. The same may be valid for "anoxic events" in the Albian, Coniacian and Santonian. The resolution of the time series used here is, however, too low to positively demonstrate a causality. Central to this is the question of how far the so-called "anoxic events" were indeed times of widespread anaerobic bottom waters. Results from recent research suggest that dysaerobic conditions may have been widespread, but that true and persistent anaerobic conditions may have been rather confined in space and time (e.g., Tyson and Pearson, 1991).

A second argument of crucial importance is the one brought forward by Delaney and Filippelli (1994). These authors used the lack of correlation between time series of Neogene phosphorus burial at selected ODP Sites in the Pacific (showing a maximum in phosphorus burial during the late Miocene–early Pliocene) and various carbon burial models mainly based on the $\partial^{13}C$ record (pointing to an apparent decrease in global marine organic carbon burial during the Neogene), to demonstrate a general decoupling of the global phosphorus and carbon cycles during the Neogene. This is an important inference, which questions the role of phosphate as a driving force behind the exogenic carbon cycle (compare Section 5.1.). There are several lines of arguments in this publication that need further scrutiny: (1) the phosphorus burial curve used here correlates rather poorly to the ones published by Delaney and Filippelli (1994) and Filippelli and Delaney (1994, Filippelli and Delaney (in press). This may be due to the small number and regional character of ODP Sites used by Delaney and Filippelli (1994; eastern and western equatorial Pacific ODP Sites 803, 804, 806, 807, 844, 846, 851). The time series from the eastern equatorial Pacific, for instance, appear to have been influenced by episodes of hydrothermal activity and phosphate-scavenging by hydrothermally derived iron oxyhydroxides (Filippelli, 1994); (2) the Neogene $\partial^{13}C$ record may not be representative of trends in organic carbon burial alone, but may rather reflect an increase in carbonate carbon burial relative to organic carbon burial (compare, for instance, Neogene carbonate burial rates given by Hay et al., 1981; Ehrmann and Thiede, 1985 and Hay, 1985); (3) absolute sediment-accumulation rates have substantially increased during the Neogene (e.g., Ehrmann and Thiede, 1985), and this alone may have led to a substantial increase in the burial of organic carbon, if we consider the empirical relationship between organic carbon burial and sediment accumulation rate (e.g., Müller and Suess, 1979; Calvert, 1987; Emerson and Hedges, 1988; Ittekkot, 1993; compare also Stein, 1991, who compiled and analyzed organic carbon burial rates for a variety of selected ODP Sites). Hay et al. (1981) have indeed shown that global organic carbon burial rates increased by more than one order of magnitude in the last 30 Myr (their compilation is based on DSDP data, but not corrected for compaction).

5.5. Phosphorus, paleoclimates and paleoecology

With the present-day, anthropogenic, acceleration of the global phosphorus cycle and its increasing impact on the environment (Section 5.2.), one may ask what ecological effects natural fluctuations in phosphate availability may have had on ancient ecosystems. In order to evaluate this, good monitors of past ecological change are needed, which can be compared in different areas. Good archives that can be used for the reconstruction of environmental change are shallow-water reef carbonates, which are the product of complex and ecologically balanced ecosystems and are highly sensitive to environmental change. In this chapter, an example is used from the northern alpine Helvetic zone, where observed ecological change has been related to changes in phosphate loading on an ancient shelf (Föllmi et al., 1994). In the latest Jurassic and early Cretaceous, a shallow-water carbonate platform developed along the northern Tethyan margin (e.g., Funk et al., 1993). In sections of the northern, Helvetic Alps in central and eastern Switzerland, as well as in western Austria, this platform system shows three different modes of platform buildup in its evolution, which occurred repeatedly and in a predictable fashion (Fig. 23):

(1) Carbonate-platform buildup dominated by reef-type organisms such as corals, rudists, chaetitids and stromatoporoids. Oolites are important constituents as well. Siliciclastics are rare and deposition of biogenic silica was uncommon. Carbonate sediment production rates were generally high, especially during highstand progradational phases ("coral-oolite mode"; late Tithonian to earliest Valanginian and early Barremian to early Aptian).

(2) Carbonate-platform buildup dominated by crinoids, associated with bryozoans, thick-shelled bivalves, brachiopods and calcified silicisponge remains. Reef-related organisms are absent and ooids occur in minor quantities (reworked?).

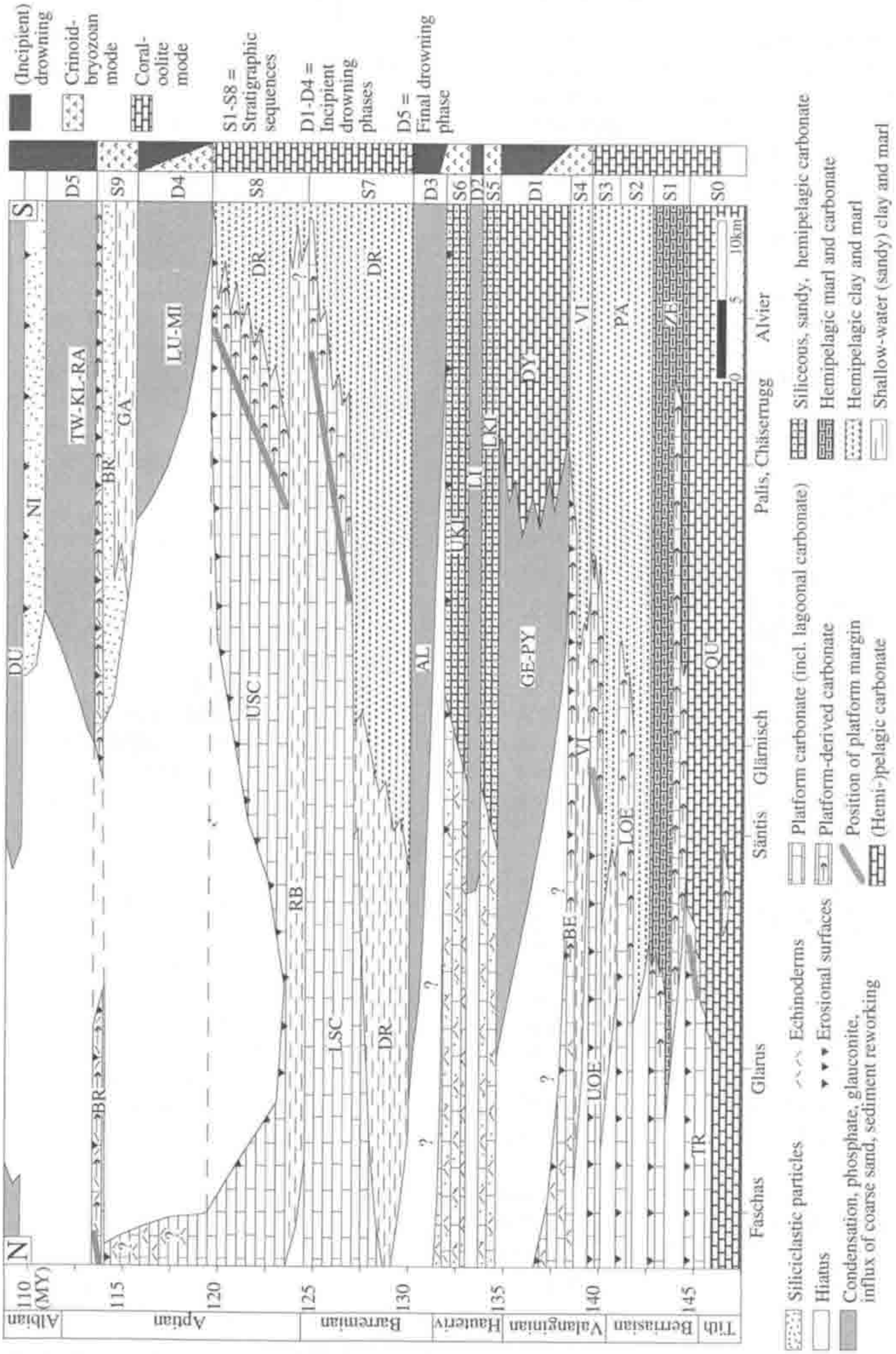


Fig. 23. Time–space diagram of a transect perpendicular to the lower Cretaceous northern Tethyan platform, reconstructed from sections exposed in the eastern part of the swiss Helvetic Alps. Proximal, landward parts are to the north and distal platform areas to the south (from Föllmi et al., 1994; reproduced with permission from the Geological Society of America).

Quartz sands are common and chert is commonly observed. Carbonate sediment production rates were very high, especially during highstand progradational phases ("crinoid–bryozoan mode"; early Valanginian, early to late Hauterivian and late Aptian).

(3) Carbonate-platform crisis, accompanied by the formation of thin and strongly condensed phosphatic crusts and layers, which lasted up to several Myr. During these crises, large areas of the carbonate platform were eroded by physical, biological and probably also chemical means.

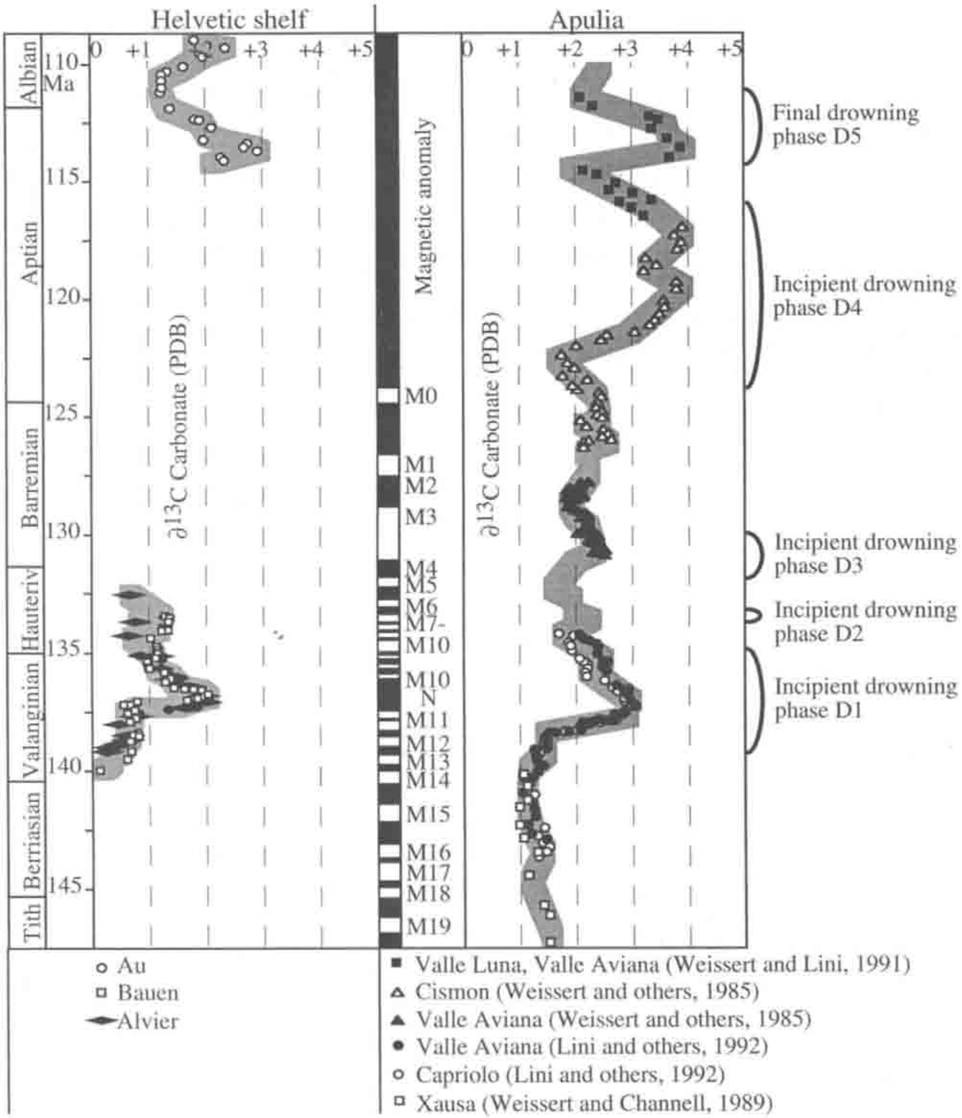


Fig. 24. Correlation of the early Cretaceous $\partial^{13}C$ record from the pelagic realm (southern Alps and Apennines) and the hemipelagic realm (northern Tethyan margin beyond the platform margin), and episodes of phosphorite formation and platform drowning in the northern Tethyan shallow-water carbonate platform system (from Föllmi et al., 1994; reproduced with permission from the Geological Society of America).

Coarse-grained quartz and glauconite sands are common in the condensed phosphatic horizons and may replace these beds in proximal directions (Fig. 24). These periods were characterized by relative sea-level rise and are identified as periods of (incipient) platform drowning ("platform destruction, condensation, and phosphogenesis mode"; early Valanginian to early Hauterivian, middle Hauterivian, late Hauterivian to early Barremian, early Aptian to middle late Aptian, and latest Aptian to earliest Albian; e.g., Schlager, 1989).

The coral–oolite mode of carbonate production was most likely associated with a warm and oligotrophic water regime, whereas the crinoid–bryozoan mode of carbonate production is attributed to a mesotrophic water regime. Mesotrophic conditions are indicated by the dominance of crinoids (fast-growing, versatile, suspension feeders) and the presence of mature quartz sands (a proxy for intense continental weathering; e.g., Weissert, 1990) and chert (a proxy for the increased presence of radiolaria and silicisponges). Phases of platform destruction, condensation, and phosphogenesis are attributed to the effect of eutrophic water conditions, which severely impeded the growth and spreading of benthic carbonate-producing organisms (compare Section 5.2.; Föllmi et al., 1994). In a temporal succession, the oligotrophic coral–oolite mode of carbonate production is usually followed by the mesotrophic mode of crinoid–bryozoan mode of carbonate production, which itself is followed by the eutrophic mode of platform destruction, condensation, and phosphogenesis. Shifts between these different modes, i.e., between different ecological systems populating the platform surface and determining the rate of carbonate production are thought to have been driven by changes in nutrient and especially phosphate concentrations in the bottom waters. This again is inferred to reflect changes in weathering intensity, in addition to the evidence given by the presence and quantity of detrital quartz.

A good indication that the regional relations reconstructed here between phosphate and ecological change were embedded in a framework of global change, is the temporal correlation between the episodes of phosphogenesis and platform drowning, positive excursions in the $\partial^{13}C$ record, and the global marine phosphorus burial record (Figs. 21 and 24). The early Cretaceous $\partial^{13}C$ record is interpreted as an indication of temporal shifts in the relative importance of carbonate carbon burial and organic carbon burial (Weissert, 1989; Lini et al., 1992; Föllmi et al., 1994; compare also Weissert and Mohr, in press). A global relation is also indicated by the synchroneity of these drowning periods and major and globally occurring episodes of platform demise (especially in the late Valanginian and Aptian; Schlager, 1989). Independently, the correlation between drowning episodes and the global marine phosphorus burial curve suggests that the periods of platform drowning were generally periods of increased phosphate availability.

The chain of events seen in the evolution of the northern Tethyan lower Cretaceous carbonate platform may have been induced by short episodes of intense flood-basalt volcanism, which may have lead to a steep positive gradient in degassing rates of primordial CO_2 (e.g., Caldeira and Rampino, 1991). This itself led to a greenhouse-induced buildup and spreading of warm and humid climate belts, a eustatic sea-level rise, and increased continental weathering (Fig. 25). Global warming prompted a temporal acceleration of the phosphorus cycle which itself led to an increase in productivity and the temporal breakdown of carbonate production in eutrophic shallow-marine areas.

It is tempting to speculate that the shift in the ratio of exported and buried organic carbon to carbonate carbon was very efficient in the removal of atmospheric CO_2, because in the process of carbonate carbon production, approximately half of the used bicarbonate is returned as CO_2 (which may — as an even stronger positive feedback — shift towards a higher CO_2 return in proportion to the amount of carbonate formed if dissolved CO_2 levels are high; Frankignoulle et al., 1994), whereas no CO_2 is returned in the case of complete organic carbon burial (e.g., Berner and Lasaga, 1989).

It appears that, under intensified greenhouse conditions, the combination of enhanced continental weathering (in taking up atmospheric CO_2) and the resulting accelerated phosphorus cycle exerted a negative feedback on climate warming (Fig. 25). This may have been quite different at times of cooling and widespread glaciation (Section 5.4.). There the cooling trend may be enhanced by the acceleration of the phosphorus cycle and correspondingly increased primary productivity. In other words, a glacially accelerated phosphorus cycle may exert a positive feedback on climate cooling (Fig. 25). In the long term, this positive feedback mechanism may become attenuated, and other mechanisms exerting a more forceful negative feedback may come into play. It is possible that chemical weathering of the mechanically derived glacial sediments becomes increasingly difficult if a certain level of cooling is reached, and sites of chemical weathering become limited because of the dimensions of continental ice covering and periglacial permafrost.

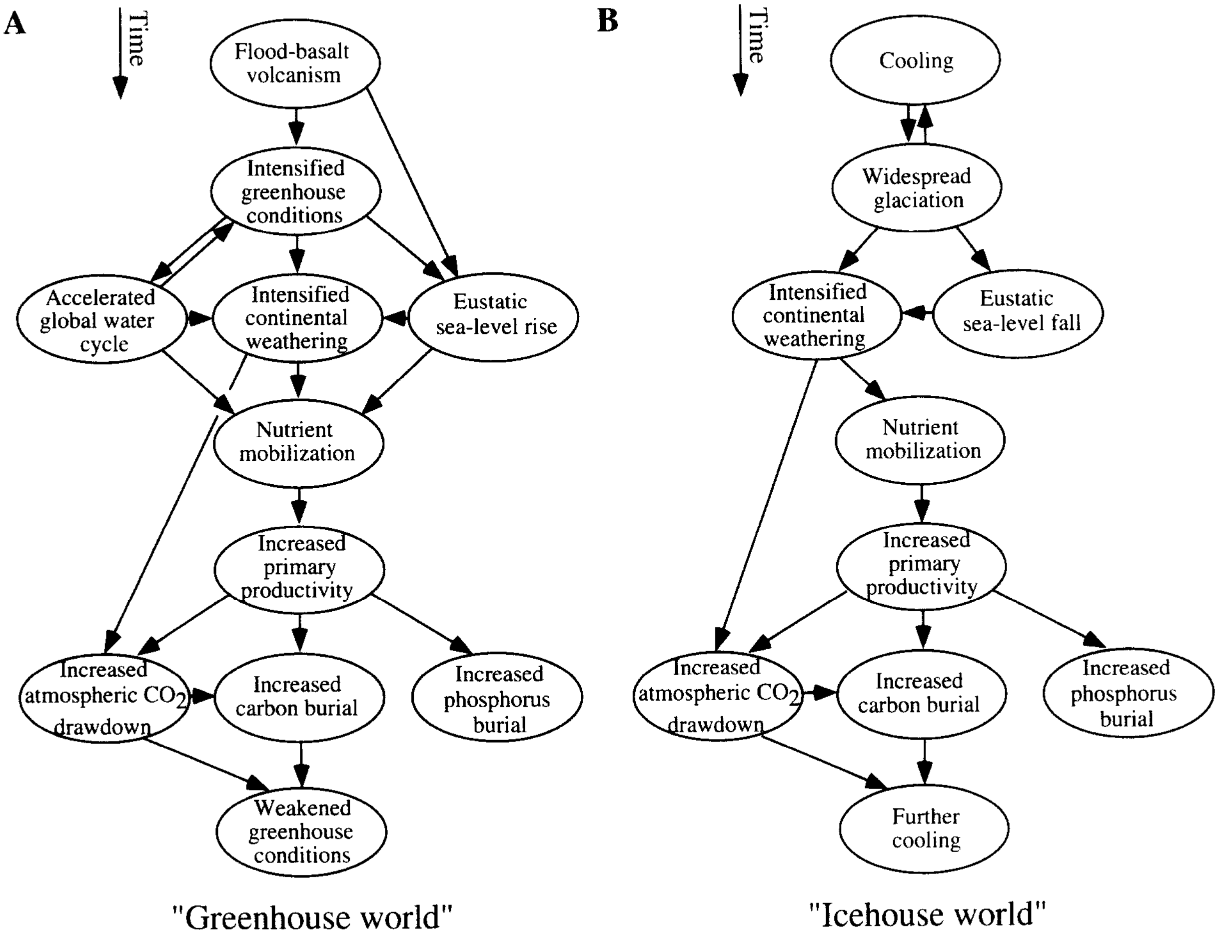


Fig. 25. Schematic representation of possible ecological and biogeochemical feedback mechanisms during (A) episodes of intensified greenhouse conditions and (B) intensified glaciation, and a correspondingly accelerated phosphorus cycle. Note that this chain of events, when triggered through flood basalt events and related greenhouse episodes, leads to cooling and phosphorus exerts a negative feedback (e.g., time between 160 and 32 Myr ago; Fig. 21), whereas, when triggered through increased glaciation, it may lead to further cooling and phosphorus may exert a positive feedback (e.g., time between 32 Myr and present, and possibly the Permian; Fig. 21) (compare Föllmi et al., 1994).

5.6. *Importance of global phosphorite "giants" through Earth's history*

The distribution of large and economically important phosphorite deposits (phosphorite "giants"; Arthur and Jenkyns, 1981; Glenn et al., 1994b) is not evenly spread through time. As noted by Cook and McElhinny (1979) and others, in certain episodes in Earth's history, conditions were more favorable to the formation of large phosphorite deposits, whereas in other periods, conditions appear less appropriate. The question to be explored here is the following: are such "giants" (1) the product of normal conditions, but considered "giant" because of exceptional preservation and good accessibility (i.e., inexpensive to exploit); (2) caused by intrinsic changes, i.e., through shifts in the relative importance of phosphate sinks in favor of authigenic sinks (Table 1); or are they caused by (3) extrinsic changes, i.e., by an increase in continental weathering rates; and are phosphorite giants, for this reason, the expression of a temporarily accelerated global phosphorus cycle? What "giant" means in terms of the global phosphorus cycle, can be shown by simple calculations. For the entire southern Tethyan phosphorite belt formed during the Paleocene and Eocene, the total amount of exploitable phosphorus is estimated to be approximately 3.4×10^{16} gP (R.P. Sheldon, Washington, pers. commun., 1992). This amount equates to the total amount of reactive phosphorus flux rates in a timespan of 6 kyr, if we take the present-day flux of reactive phosphate (5.7×10^{12} gP/yr; Fig. 1) and assume a complete transformation into phosphorite. The total amount of exploitable phosphorus in the Permian Phosphoria Formation has been estimated as high as 7×10^{17} gP, which would correspond to approximately 120 kyr if all of the present-day reactive phosphate flux would be available for phosphorite formation (Arthur and Jenkyns, 1981). Ruttenberg (1993) estimated that nearly 50% of the total input of reactive phosphate is extracted from the marine living biosphere through phosphogenesis and the growth of fish hard parts (Table 1). If this ratio is extrapolated to the two examples used here, 12 and 240 kyr is needed to form the phosphorites of the southern Tethyan Paleocene and Eocene province, and the Permian Phosphoria Formation, respectively, under the assumption that phosphorite formation is not taking place elsewhere at the same time. This example shows that, with regards to time, no extraordinary conditions are needed in order to accumulate phosphorite in economically attractive amounts (compare also Filippelli and Delaney, 1992).

On the other hand, it appears that during times of an accelerated phosphorus cycle, paleoceanographic and sedimentary conditions may favor major phosphorite formation (Fig. 25). In the case the phosphorus cycle becomes accelerated under reinforced greenhouse conditions, cells of coastal upwelling may increase in size and number, due to increased wind circulation (Bakun, 1990), sea level may rise, and sedimentary conditions may be created in outer shelf and slope environments which are appropriate for phosphorite formation (shifts of geostrophic currents onto the outer shelf, lowering of sediment-accumulation rates, etc.; compare Sections 3.4., 4.2. and 4.3.). In times of cooling, the increase in latitudinal temperature gradients may lead to more intensified oceanic circulation and increased coastal upwelling, which itself may lead to a greater phosphate flux to outer-shelf sediments (e.g., Vincent and Berger, 1985).

A comparison of the marine phosphorus burial curve (Figs. 18 and 19) with the occurrence of economically viable phosphorite deposits through time (i.e., Mid-Cretaceous, Santonian–Campanian, Paleocene–Eocene, early and middle Miocene; e.g., Föllmi et al., 1993) suggests that during times of an accelerated phosphorus cycle, phosphorite formation is indeed favored. Most phosphorite "giants" can, for these reasons, be considered the result of a chain of extraordinary sedimentological and paleoenvironmental conditions, which resulted from periods of global climate change.

6. Outlook

It is its capacity as an essential nutrient and energy carrier that renders phosphorus a key element in the biosphere, where it mediates between living and lifeless compartments by feedback. The availability of phosphorus (as phosphate) is modulated by changes in rates of continental weathering and, therefore, by climate change. Climate patterns change almost predictably in response to the extrinsic cycles of change in astronomic parameters ("Milankovitch cycles"; on a kyr-time scale), or intrinsic cycles of intensity in mantle upwelling and sea-floor spreading (on a Myr-time scale). Superimposed on these climate rhythms are the dramatic effects of stochastic events such as bolide impact and plate-boundary reorganizational phases combined with extensive flood basalt formation. It appears that these episodes of reinforced climate change had the greatest impact on the global phosphorus cycle. In times of rapid and major climate change, the availability of reactive phosphate increased by one order of magnitude. This phosphate surplus severely affected terrestrial and marine ecosystems, as can be seen from a general increase in productivity rates (and organic matter deposition) and the breakdown of carbonate-producing benthic organisms in shallow-marine environments adjacent to continents (platform drowning). In phases of warm climate and high atmospheric CO_2, the combination of increased continental weathering and increased productivity may have led to an effective drawdown of atmospheric CO_2 and phosphate may have exerted a negative feedback. By contrast, during times of major cooling and spreading of glacially induced weathering, the temporal increase in phosphate may have led to a positive feedback on climate development, which probably could only be halted by the progressive development of glacial conditions and a corresponding decrease in chemical weathering. Unlike most other chemical elements, the function of phosphate in the biosphere can be judged as that of a potent chemical messenger in mediating between physically induced climate changes and the living part of the biosphere, through the regulation of the global carbon cycle.

The study of phosphates and phosphorites in marine sediments adds another dimension to our knowledge of the global phosphorus cycle. In locating the sites of major phosphogenesis and phosphorite accumulation, in studying the physical and biogeochemical processes leading to phosphogenesis, and in interpreting the type of stratification and sedimentary architecture of the phosphorite deposit, much knowledge comes together which helps to understand the sedimentological, paleoecological, biogeochemical and paleoceanographic conditions under which they formed. If we take into account that major phosphorite deposits formed during episodes in Earth's history distinguished by steep gradients in the development of climate and ecology, research focused on such deposits may very much help to improve our understanding of the processes operating during these periods of global change. Furthermore, the statistical exploration and comparison of phosphorus accumulation rates in representative basins in selected time windows give additional, general and quantitative, information on changes in continental weathering rates and related changes in climate.

It is clear from the above, that phosphorus is beneficial to the biosphere in many ways; however, examples from the present and the geological past also show that phosphorus may be deleterious to large parts of the biosphere when released and applied above natural thresholds levels. Through the excessive use of phosphorus, an intricate network of feedback mechanisms comes into play, a play that may evolve into a drama, if we look at the present-day anthropogenic release rates of phosphorus and the already visible impact on ecosystems. Here, phosphorus is receiving just a fraction of the attention that is directed towards the carbon cycle, in spite of the close and crucial relations between the two cycles; indeed and most urgently, more concern is needed, both in the case of direct environmental consequences resulting from phosphorus exploitation and application, as well as in the case of short- and long-term ecological changes due to general anthropogenic phosphate overloading.

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Karl B. Föllmi received his diploma, doctoral, and habilitation degrees from the ETH, Zürich, where he currently is a research scientist and docent. He started as a classical stratigrapher and paleontologist working in mid-Cretaceous sediments. During his postdoctoral stay at the University of California in Santa Cruz (1987–1989), he turned his interest towards sedimentology, paleoceanography and -climatology, and geochemistry, and worked in sediments of late Cretaceous to Holocene age. Presently he is interested in the coupling of the phosphorus and carbon cyecle, the effecnt of global variations in nutrient availabilit, the importance of continent–ocean links, and the reconstruction of paleoclimatic and paleoenvironmental conditions in general.