

8.13

The Global Phosphorus Cycle

K. C. Ruttenberg

University of Hawaii at Manoa, Honolulu, HI, USA

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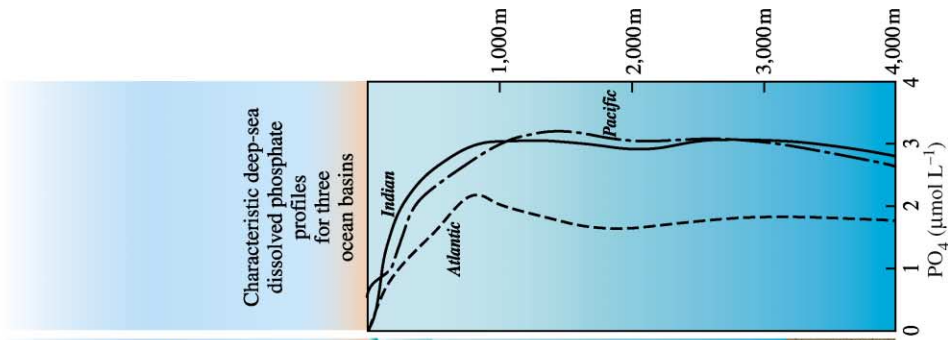
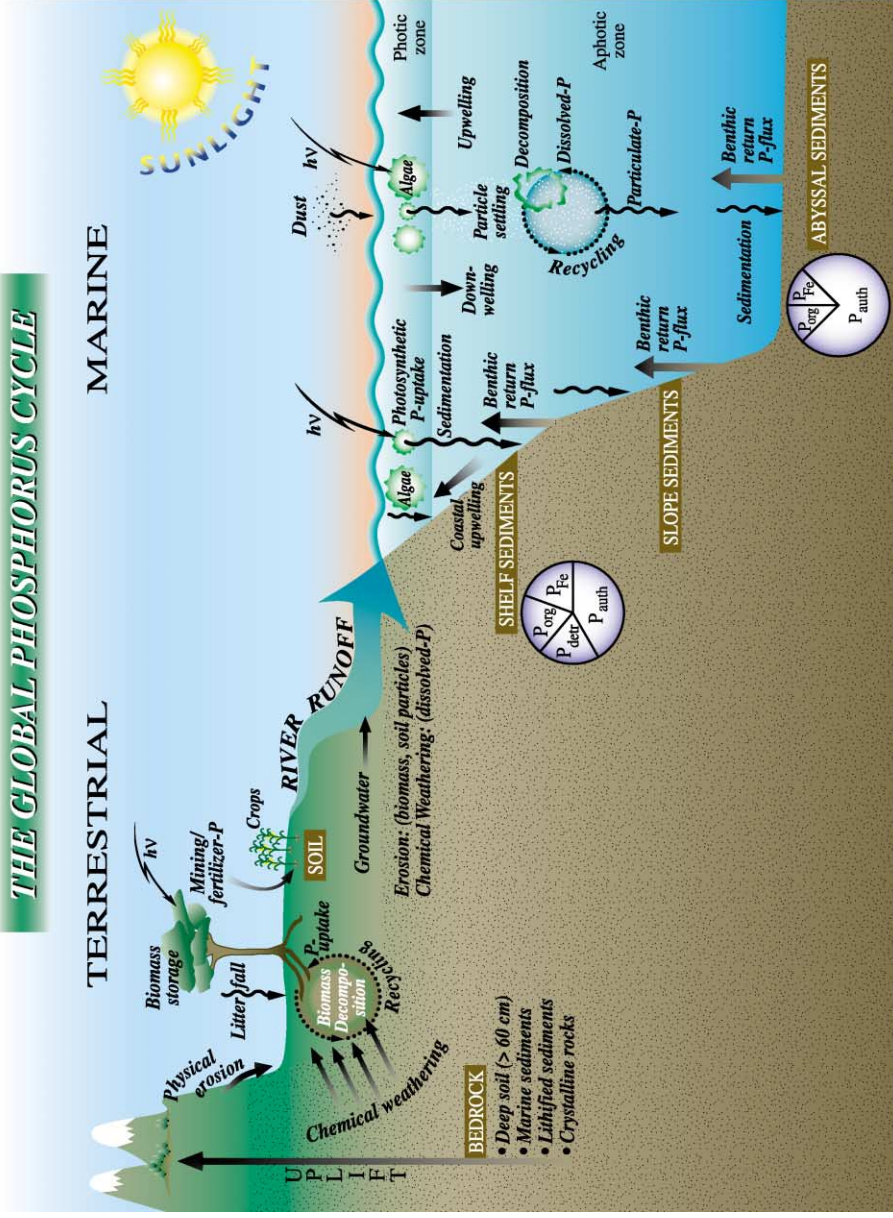
8.13.1 INTRODUCTION

Phosphorus is an essential nutrient for all life forms. It is a key player in fundamental biochemical reactions (Westheimer, 1987) involving genetic material (DNA, RNA) and energy transfer (ATP), and in structural support of organisms provided by membranes (phospholipids) and bone (the biomineral hydroxyapatite). Photosynthetic organisms utilize dissolved phosphorus, carbon, and other essential nutrients to build their tissues using energy from the Sun. Biological productivity is contingent upon the availability of phosphorus to these simple organisms that constitute the base of the food web in both terrestrial and aquatic systems. (For reviews of P-utilization, P-biochemicals, and pathways

in aquatic plants, see Fogg (1973), Bielecki and Ferguson (1983), and Cembella *et al.* (1984a, 1984b).)

Phosphorus locked up in bedrock, soils, and sediments is not directly available to organisms. Conversion of unavailable forms to dissolved orthophosphate, which can be directly assimilated, occurs through geochemical and biochemical reactions at various stages in the global phosphorus cycle. Production of biomass fueled by P-bioavailability results in the deposition of organic matter in soils and sediments, where it acts as a source of fuel and nutrients to microbial communities. Microbial activity in soils and sediments, in turn, strongly influences the concentration and chemical form of phosphorus incorporated into the geological record.

THE GLOBAL PHOSPHORUS CYCLE



The global phosphorus cycle has four major components: (i) tectonic uplift and exposure of phosphorus-bearing rocks to the forces of weathering; (ii) physical erosion and chemical weathering of rocks producing soils and providing dissolved and particulate phosphorus to rivers; (iii) riverine transport of phosphorus to lakes and the ocean; and (iv) sedimentation of phosphorus associated with organic and mineral matter and burial in sediments (Figure 1). The cycle begins anew with uplift of sediments into the weathering regime.

This chapter begins with a brief overview of the various components of the global phosphorus cycle. Estimates of the mass of important phosphorus reservoirs, transport rates (fluxes) between reservoirs, and residence times are given in Tables 1 and 2. As is clear from the large uncertainties associated with these estimates of reservoir size and flux, many aspects of the global phosphorus cycle remain poorly understood. Following the overview, various aspects of the global phosphorus cycle will be examined in more depth, including a discussion of the most pressing research questions currently being posed, and research efforts presently underway to address these questions.

8.13.2 THE GLOBAL PHOSPHORUS CYCLE: OVERVIEW

8.13.2.1 The Terrestrial Phosphorus Cycle

In terrestrial systems phosphorus resides in three pools: bedrock, soil, and living organisms (biomass) (Table 1). Weathering of continental bedrock is the principal source of phosphorus to the soils that support continental vegetation (F_{12}); atmospheric deposition is relatively unimportant (F_{82}). Phosphorus is weathered from bedrock by dissolution of phosphorus-bearing minerals such as apatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{F},\text{Cl})_2$), the most

abundant primary P-mineral in crustal rocks. Weathering reactions are driven by exposure of minerals to naturally occurring acids derived mainly from microbial activity (e.g., Cosgrove, 1977; Frossard *et al.*, 1995). Phosphate solubilized during weathering is available for uptake by terrestrial plants, and is returned to the soil by decay of litterfall (e.g., Likens *et al.*, 1977).

Soil solution phosphate is maintained at low levels as a result of P-sorption by various soil constituents, particularly ferric iron and aluminum oxyhydroxides. Sorption is considered the most important process controlling terrestrial P-bioavailability (Lajtha and Harrison, 1995). Plants have different physiological strategies for obtaining P-despite low soil solution concentrations. For example, some plants can increase root volume and surface area to optimize uptake potential. Alternatively, plant roots and/or associated fungi can produce (i) chelating compounds that solubilize ferric iron, aluminum, and calcium-bound phosphorus, (ii) enzymes and/or (iii) acids in the root vicinity, to solubilize phosphate (Lajtha and Harrison, 1995). Plants also minimize P-loss by resorbing much of their phosphorus prior to litterfall, and by efficient recycling from fallen litter. In extremely unfertile soils (e.g., in tropical rain forests) P-recycling is so efficient that topsoil contains virtually no phosphorus; it is all tied up in biomass (e.g., Vitousek *et al.*, 1997).

Systematic changes in the total amount and chemical form of phosphorus occur during soil development. In initial stages, phosphorus is present mainly as primary minerals such as apatite. In mid-stage soils, the reservoir of primary apatite is diminished; less-soluble secondary minerals and organic-P make up an increasing fraction of soil phosphorus. Late in soil development, phosphorus is partitioned mainly between refractory minerals and organic-P (Figure 2). This classic model articulated by Walker and Syers (1976) has been validated in

Figure 1 The major reservoirs and fluxes of the global phosphorus cycle are illustrated (see Tables 1 and 2, and text). The oceanic photic zone, idealized in the cartoon, is typically thinner in coastal environments due to turbidity from continental terrigenous input, and deepens as the water column clarifies with distance away from the continental margins. The distribution of phosphorus among different chemical/mineral forms in marine sediments is given in the pie diagrams, where the abbreviations used are: organic phosphorus (P_{org}), iron-bound phosphorus (P_{Fe}), detrital apatite (P_{detr}), authigenic/biogenic apatite (P_{auth}). The P_{org} , P_{Fe} , and P_{auth} reservoirs represent potentially reactive-P pools (see text and Tables 2 and 3 for discussion), whereas the P_{detr} pool reflects mainly detrital apatite weathered off the continents and passively deposited in marine sediments (note that P_{detr} is not an important sedimentary phosphorus component in abyssal sediments, far from continents). Continental margin P-speciation data were compiled from Louchouart *et al.* (1997), and Ruttenberg and Berner (1993). Abyssal sediment P-speciation data were compiled from Filippelli and Delaney (1996), and Ruttenberg (1990). The “global phosphorus cycle” cartoon is from Ruttenberg (2002). The vertical water column phosphate distributions typically observed in the three ocean basins are shown in the panel to the right of the “global phosphorus cycle” cartoon, and are from Sverdrup *et al.* (1942).

Table 1 Major reservoirs active in the global phosphorus cycle and associated residence times.

| <i>Reservoir #</i> | <i>Reservoir description</i> | <i>Reservoir size</i> (mole P $\times 10^{12}$) | <i>Reference</i> | <i>Residence time</i> τ (yr) |
|--------------------|---|---|------------------|--------------------------------------|
| R1 | Sediments (crustal rocks and soil >60 cm deep and marine sediments) | $0.27 \times 10^8 - 1.3 \times 10^8$ | b, a = c = d | $42 - 201 \times 10^6$ |
| R2 | Land (\approx total soil <60 cm deep: organic + inorganic) | 3,100–6,450 | b, a = c = d | 425–2,311 |
| R3 | Land biota | 83.9–96.8 | b, a = c = d | 13–48 |
| R4 | Surface ocean, 0–300 m (total dissolved P) | 87.4 | a = c | 2.46–4.39 |
| R5 | Deep sea, 300–3300 m (total dissolved P) | 2,810 | a = c & d | 1,502 |
| R6 | Oceanic biota | 1.61–4.45 | b & d, a = c & d | 0.044–0.217 (16–78 d) |
| R7 | Minable P | 323–645 | a = c, b & d | 718–1,654 |
| R8 | Atmospheric P | 0.0009 | b = c = d | 0.009 (80 h) |

(1) Ranges are reported for those reservoirs for which a consensus on a single best estimated reservoir size does not exist. Maximum and minimum estimates found in a survey of the literature are reported. References cited before the comma refer to the first (lowest) estimate, those after the comma refer to the second (higher) estimate. References that give identical values are designated by an equality sign, references giving similar values are indicated by an ampersand. As indicated by the wide ranges reported for some reservoirs, all calculations of reservoir size have associated with them a large degree of uncertainty. Methods of calculation, underlying assumptions, and sources of error are given in the references cited.

(2) Residence times are calculated by dividing the concentration of phosphorus contained in a given reservoir by the sum of fluxes out of the reservoir. Where ranges are reported for reservoir size and flux, maximum and minimum residence time values are given; these ranges reflect the uncertainties inherent in reservoir size and flux estimates. Fluxes used to calculate residence times for each reservoir are as follows: R1 (F_{12}), R2 ($F_{23} + F_{28} + F_{24(d)} + F_{24(p)}$), R3 (F_{32}), R4 ($F_{45} + F_{46}$), R5 (F_{54}), R6 ($F_{64} + F_{65}$), R7 (F_{72}), R8 ($F_{82} + F_{84}$). Flux estimates are given in Table 2. The residence time of R5 is decreased to 1,492 yr by inclusion of the scavenged flux of deep-sea phosphate at hydrothermal MOR systems, mostly onto ferric oxide and oxyhydroxide phases (Wheat *et al.* (1996)).

(3) Estimates for the partitioning of the oceanic reservoir between dissolved inorganic phosphorus and particulate phosphorus are given in references b and d as follows: $(2,581 - 2,600) \times 10^{12}$ mol dissolved inorganic phosphorus (b, d) and $(20 - 21) \times 10^{12}$ mol particulate phosphorus (d, b).

(4) The residence times estimated for the minable phosphorus reservoir reflect estimates of current mining rates; if mining activity increases or diminishes the residence time will change accordingly.

^a Lerman *et al.* (1975) ^b Richey (1983) ^c Jahnke (1992) ^d Mackenzie *et al.* (1993).

Table 2 Fluxes between the major phosphorus reservoirs.

| <i>Flux #</i> | <i>Description of flux</i> | <i>Flux</i> (moles P × 10 ¹² yr ⁻¹) | <i>References and comments</i> |
|------------------------------|---|---|--|
| <i>Reservoir fluxes:</i> | | | |
| <i>F</i> ₁₂ | rocks/sediments → soils (erosion/weathering, soil accumulation) | 0.645 | a = c&d |
| <i>F</i> ₂₁ | soils → rocks/sediments (deep burial, lithification) | 0.301–0.603 | d, a = c |
| <i>F</i> ₂₃ | soils → land biota | 2.03–6.45 | a = c, b&d |
| <i>F</i> ₃₂ | land biota → soils | 2.03–6.45 | a = c, b&d |
| <i>F</i> _{24(d)} | soil → surface ocean (river total dissolved P flux) | 0.032–0.058 | e, a = c; ca. >50% of TDP is DOP (e) |
| <i>F</i> _{24(p)} | soil → surface ocean (river particulate P flux) | 0.59–0.65 | d, e; ca. 40% of RSPM-P is org. P (e); it is estimated that between 25% and 45% is reactive once it enters the ocean (f). |
| <i>F</i> ₄₆ | surface ocean → oceanic biota | 19.35–35 | b, d; a = c = 33.5, b reports upper limit of 32.3; d reports lower limit of 28.2 |
| <i>F</i> ₆₄ | oceanic biota → surface ocean | 19.35–35 | b,d; a&c = 32.2, b reports upper limit of 32.3; d reports lower limit of 28.2 |
| <i>F</i> ₆₅ | oceanic biota → deep sea (particulate rain) | 1.13–1.35 | d, a = c |
| <i>F</i> ₄₅ | surface ocean → deep sea (downwelling) | 0.581 | a = c |
| <i>F</i> ₅₄ | deep sea → surface ocean (upwelling) | 1.87 | a = c |
| <i>F</i> ₄₂ | surface ocean → land (fisheries) | 0.01 | d |
| <i>F</i> ₇₂ | minable P → land (soil) | 0.39–0.45 | a = c = d, b |
| <i>F</i> ₂₈ | land (soil) → atmosphere | 0.14 | b = c = d |
| <i>F</i> ₈₂ | atmosphere → land (soil) | 0.1 | b = c = d |
| <i>F</i> ₄₈ | surface ocean → atmosphere | 0.01 | b = c = d |
| <i>F</i> ₈₄ | atmosphere → surface ocean | 0.02–0.05 | c, b; d gives 0.04; ca. 30% of atmospheric aerosol-P is soluble (g) |
| <i>Sub-reservoir fluxes:</i> | | | |
| <i>marine sediments</i> | | | |
| sF _{ms} | marine sediment accumulation (total) | 0.265–0.280 | i, j; for higher estimate (j), use of sediment P-concentration below the diagenesis zone implicitly accounts for P-loss via benthic remineralization flux and yields pre-anthropogenic net burial flux. For estimates of reactive-P burial see note (j). |

(continued)

Table 2 (continued).

| <i>Flux #</i> | <i>Description of flux</i> | <i>Flux</i> (moles P × 10 ¹² yr ⁻¹) | <i>References and comments</i> |
|-------------------|--|---|---|
| sF _{cs} | continental margin ocean sediments → burial | 0.150–0.223 | j, i; values reported reflect total-P, reactive-P burial constitutes from 40% to 75% of total-P (h). These values reflect pre-agricultural fluxes, modern value estimated as 0.33 (d). |
| sF _{as} | abyssal (deep sea) sediments → burial | 0.042–0.130 | i, j; a = c gives a value of 0.055. It is estimated that 90–100% of this flux is reactive-P (h). These values reflect pre-agricultural fluxes, modern value estimates range from 0.32 (d) to 0.419 (b). |
| sF _{cbf} | coastal sediments → coastal waters (rem mineralization, benthic flux) | 0.51–0.84 | d, k; these values reflect pre-agricultural fluxes, modern value estimated as 1.21 with uncertainties ±40% (k). |
| sF _{abf} | abyssal sediments → deep sea (rem mineralization, benthic flux) | 0.41 | k; this value reflects pre-agricultural fluxes, modern value estimated as 0.52, uncertainty ±30% (k) |

(1) Reservoir fluxes (*F*) represent the P-flux between reservoirs #R1–R8 defined in Table 1. The sub-reservoir fluxes (sF) refer to the flux of phosphorus into the marine sediment portion of reservoir #1 via sediment burial, and the flux of diagenetically mobilized phosphorus out of marine sediments via benthic return flux. These sub-fluxes have been calculated as described in references h–k. Note that the large magnitude of these sub-fluxes relative to those into and out of reservoir #1 as a whole, and the short oceanic-P residence time they imply (Tables 1 and 5), highlight the dynamic nature of the marine phosphorus cycle.

(2) Ranges are reported where consensus on a single best estimate does not exist. References cited before the comma refer to the first (lower) estimate, those after the comma refer to the second (higher) estimate. References that give identical values are designated by an equality sign, references giving similar values are indicated by an ampersand. Maximum and minimum estimates found in a survey of the literature are reported. In some cases this range subsumes ranges reported in the primary references. As indicated by the wide ranges reported, all flux calculations have associated with them a large degree of uncertainty. Methods of calculation, underlying assumptions, and sources of error are given in the references cited.

^a Lerman, *et al.* (1975) ^b Richey (1983) ^c Jahnke (1992) ^d Mackenzie *et al.* (1993) ^e Meybeck (1982)

^f The range of riverine suspended particulate matter that may be solubilized once it enters the marine realm (e.g., the so-called “reactive-P”) is derived from three sources. Colman and Holland (2000) estimate that 45% may be reactive, based on RSPM-P compositional data from a number of rivers and estimated burial efficiency of this material in marine sediments. Berner and Rao (1994) and Ruttenberg and Canfield (1994) estimate that 35% and 31% of RSPM-P is released upon entering the ocean, based on comparison of RSPM-P and adjacent deltaic surface sediment phosphorus in the Amazon and Mississippi systems, respectively. Lower estimates have been published (8%: Ramirez and Rose (1992); 18%: Froelich (1988); 18%: Compton *et al.* (2000). Higher estimates have also been published (69%: Howarth *et al.* (1995).

Howarth *et al.* (1995) also estimate the total flux of riverine particulate phosphorus to the oceans at 0.23×10^{12} moles P yr⁻¹, an estimate likely too low because it uses the suspended sediment flux from Milliman and Meade (1983), which does not include the high sediment flux rivers from tropical mountainous terranes (Milliman and Syvitski (1992). ^g Duce *et al.* (1991) ^h Ruttenberg (1993) ⁱ Howarth *et al.* (1995) ^j P-burial flux estimates as reported in Ruttenberg (1993) modified using pre-agricultural sediment fluxes updated by Colman and Holland (2000). Using these total P burial fluxes and the ranges of likely reactive P given in the table, the best estimate for reactive P burial flux in the oceans lies between $(0.177–0.242) \times 10^{12}$ moles P yr⁻¹. Other estimates of whole-ocean reactive P burial fluxes range from, at the low end: 0.032 to 0.081×10^{12} moles P yr⁻¹ (Compton *et al.* (2000), and 0.09×10^{12} moles P yr⁻¹ (Wheat *et al.* (1996); to values more comparable to those derived from the table above (0.21×10^{12} moles P yr⁻¹: Filippelli and Delany (1996). ^k Colman and Holland (2000).

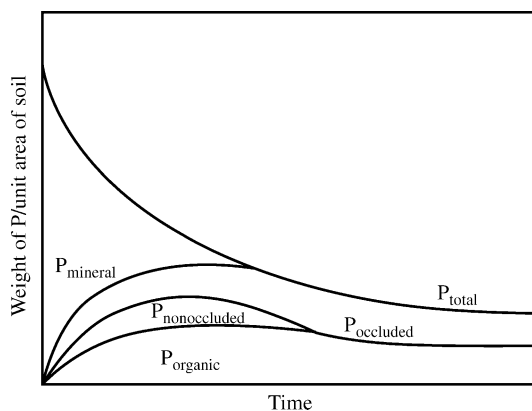


Figure 2 The fate of phosphorus during soil formation can be viewed as the progressive dissolution of primary mineral phosphorus (dominantly apatite), some of which is lost from the system by leaching (decrease in P_{total}), and some of which is reincorporated into nonoccluded, occluded, and organic fractions within the soil. Non-occluded phosphorus is defined as phosphate sorbed to surfaces of hydrous oxides of iron and aluminum, and calcium carbonate. Occluded phosphorus refers to phosphorus present within the mineral matrix of discrete mineral phases. The initial buildup in organic phosphorus results from organic matter return to soil from vegetation supported by the soil. The subsequent decline in P_{organic} is due to progressive mineralization and soil leaching. The timescale over which these transformations occur depends upon the initial soil composition, topographic, and climatic factors (after Walker and Syers, 1976).

numerous subsequent works (e.g., Smeck, 1985; Lajtha and Schlesinger, 1988; Crews *et al.*, 1995; Schlesinger *et al.*, 1998; Filippelli and Souch, 1999; Chadwick *et al.*, 1999).

8.13.2.2 Transport of Phosphorus from Continents to the Ocean

Phosphorus is transferred from the continental to the oceanic reservoir primarily by rivers (F_{24}). Deposition of atmospheric aerosols (F_{84}) is a minor flux. Groundwater seepage to the coastal ocean is a potentially important but poorly documented flux. Riverine phosphorus derives from weathered continental rocks and soils. Because phosphorus is particle reactive, most riverine-P is associated with particulate matter. By most estimates, well over 90% of the phosphorus delivered by rivers to the ocean is as particulate-P ($F_{24(p)}$). Dissolved phosphorus in rivers occurs in both inorganic and organic forms. The scant data on dissolved organic P suggest that it may account for 50% or more of dissolved riverine-P (Meybeck, 1982). The chemical form of phosphorus associated with riverine particles is variable and depends upon the drainage basin geology, extent of weathering of the substrate,

and on the nature of the river itself. Available data suggest that ~20–40% of phosphorus in suspended particulate matter is organic; inorganic forms are partitioned mainly between ferric oxyhydroxides and apatite (Lucotte and d'Anglejan, 1983; Lebo, 1991; Berner and Rao, 1994; Ruttenberg and Canfield, 1994). Aluminum oxyhydroxides and clays may also be significant carriers of phosphorus (Lebo, 1991).

The fate of phosphorus entering the ocean via rivers is variable. Dissolved phosphorus in estuaries at the continent–ocean interface typically displays nonconservative behavior. Both negative and positive deviations from conservative mixing can occur, sometimes changing seasonally within the same estuary (Froelich *et al.*, 1982; Fox *et al.*, 1985, 1986, 1987). Net removal of phosphorus in estuaries is typically driven by flocculation of humic–iron complexes and biological uptake (e.g., Sholkovitz *et al.*, 1978; Fox, 1990). Net P-release is due to a combination of desorption from freshwater particles entering high ionic strength marine waters, and flux of diagenetically mobilized phosphorus from benthic sediments (e.g., Chase and Sayles, 1980; Nixon, 1981; Nixon and Pilson, 1984; Fox *et al.*, 1986; Berner and Rao, 1994; Chambers *et al.*, 1995; Conley *et al.*, 1995). Accurate estimates of bioavailable riverine-P flux to the ocean must take into account, in addition to dissolved forms, the fraction of riverine particulate-P released to solution upon entering the ocean (Tables 2 and 3).

8.13.2.2.1 Human impacts on the global phosphorus cycle

The mining of phosphate rock (mostly from terrestrially emplaced marine phosphorite deposits) for use as agricultural fertilizer has increased dramatically in the latter half of this century (F_{72}). In addition to fertilizer use, deforestation, increased cultivation, urban and industrial waste disposal all have enhanced phosphorus transport from terrestrial to aquatic systems, often with deleterious results. For example, elevated phosphorus concentrations in rivers resulting from these activities have resulted in eutrophication in some lakes and coastal areas, stimulating nuisance algal blooms and promoting hypoxic or anoxic conditions harmful or lethal to natural populations (e.g., Caraco, 1995; Fisher *et al.*, 1995; Melack, 1995).

Increased erosion due to forest clear-cutting and widespread cultivation has increased riverine suspended matter concentrations, and thus increased the riverine particulate-P flux. Dams, in contrast, decrease sediment loads in rivers and therefore diminish the phosphorus flux to the oceans. However, increased erosion below dams

Table 3 Revised oceanic phosphorus input fluxes, removal fluxes, and estimated oceanic residence time.

| Flux description ^a | | Flux (moles P × 10 ¹² yr ⁻¹) | Residence time ^e (yr) |
|-------------------------------|---|--|-------------------------------------|
| <i>Input fluxes:</i> | | | |
| F_{84} | atmosphere → surface ocean | 0.02–0.05 | |
| $F_{24(d)}$ | soil → surface ocean (river dissolved P flux) ^b | 0.032–0.058 | |
| $F_{24(p)}$ | soil → surface ocean (river particulate P flux) ^b | 0.59–0.65 | |
| | Minimum reactive-P input flux | 0.245 | 12,000 |
| | Maximum reactive-P input flux | 0.301 | 10,000 |
| <i>Removal fluxes:</i> | | | |
| sF_{cs} | Best estimate of total-P burial in continental margin marine sediments (Table 2, note j) ^c | 0.150 | |
| sF_{as} | Best estimate of total-P burial in abyssal marine sediments (Table 2, note j) ^c | 0.130 | |
| | Minimum estimate of reactive-P burial in marine sediments ^d | 0.177 | 17,000 |
| | Maximum estimate of reactive-P burial in marine sediments ^d | 0.242 | 12,000 |

^a All fluxes are from Table 2. ^b As noted in Table 2, 30% of atmospheric aerosol-P (Duce *et al.*, 1991) and 25–45% of the river particulate flux (see note (f) in Table 2) is believed to be mobilized upon entering the ocean. The reactive-P input flux was calculated as the sum of $0.3(F_{84}) + F_{24(d)} + 0.35(F_{24(p)})$, where the mean value of the fraction of riverine particulate phosphorus flux estimated as reactive-P (35%) was used. Reactive-P is defined as that which passes through the dissolved oceanic P-reservoir, and thus is available for biological uptake. ^c These estimates are favored by the author, and reflect the minimum sF_{cs} and maximum sF_{as} fluxes given in Table 2. Because the reactive-P content of continental margin and abyssal sediments differs (see Table 2 and note d, below), these fluxes must be listed separately in order to calculate the whole-ocean reactive-P burial flux. See note (j) in Table 2 for other published estimates of reactive-P burial flux. ^d As noted in Table 2, between 40% and 75% of phosphorus buried in continental margin sediments is potentially reactive, and 90% to 100% of phosphorus buried in abyssal sediments is potentially reactive. The reactive-P fraction of the total sedimentary P-reservoir represents that which may have passed through the dissolved state in oceanic waters, and thus represents a true P-sink from the ocean. The minimum reactive-P burial flux was calculated as the sum of $0.4(sF_{cs}) + 0.9(sF_{as})$; the maximum reactive-P burial flux was calculated as the sum of $0.75(sF_{cs}) + 1(sF_{as})$. Both the flux estimates and the percent reactive-P estimates have associated with them large uncertainties. ^e Residence time estimates are calculated as the oceanic phosphorus inventory (reservoirs #4 and 5 (Table 1) = 3×10^{15} moles P) divided by the minimum and maximum input and removal fluxes.

and diagenetic mobilization of phosphorus in sediments trapped behind dams moderates this effect. The overall effect has been a 50% to threefold increase in riverine-P flux to the oceans above pre-agricultural levels (Melack, 1995; Howarth *et al.*, 1995).

8.13.2.3 The Marine Phosphorus Cycle

Phosphorus in its simplest form, dissolved orthophosphate, is taken up by photosynthetic organisms at the base of the marine food web. The marine phosphorus (P) cycle is linked to the marine carbon (C) and nitrogen (N) cycles through the photosynthetic fixation of these elements by the microscopic floating marine plants, or phytoplankton, which form the base of the marine food web. In the seminal work of Alfred Redfield (1958; Redfield *et al.*, 1963), it was recognized that marine phytoplankton, on average, have a C : N : P molar ratio of 106C : 16N : 1P. This ratio can vary due to such factors as nutrient availability and nutritive state of the phytoplankton, but the relative consistency of this ratio is striking. Further, Redfield (1958) and Redfield *et al.* (1963) pointed out that the ratio of inorganic dissolved C : N : P in seawater (as HCO_3^- , NO_3^- ,

HPO_4^{2-}) is 1,000 : 15 : 1, when contrasted with the average oceanic phytoplankton C : N : P, suggests that limitation of marine phytoplankton is poised closely between N- and P-limitation. When phosphate is exhausted, however, organisms may utilize more complex forms by converting them to orthophosphate via enzymatic and microbiological reactions (e.g., Karl and Bjorkman, 2000; Sections 8.13.3.3.3 and 8.13.3.3.4); the same is true for nitrogen. Thus, the simple, though elegant formulation of Redfield is now believed to be substantially more complex, given the role of dissolved organic nutrients in supporting marine biological productivity. In the open ocean most phosphorus associated with biogenic particles is recycled within the upper water column. Efficient stripping of phosphate from surface waters by photosynthesis combined with buildup at depth due to respiration of biogenic particles results in the classic oceanic dissolved nutrient profile. The progressive accumulation of respiration-derived phosphate at depth along the deep-water circulation trajectory results in higher phosphate concentrations in Pacific Ocean deep waters at the end of the trajectory than in the North Atlantic where deep water originates (Figure 1).

The sole means of phosphorus removal from the oceans is burial with marine sediments

(Froelich *et al.*, 1982; Ruttenberg, 1993; Delaney, 1998). The P-flux to shelf and slope sediments is larger than the P-flux to the deep sea (Table 2) for several reasons. Coastal waters receive continentally derived nutrients via rivers (including P, N, Si, Fe), which stimulate high rates of primary productivity relative to the deep sea, and result in a higher flux of organic matter to continental margin sediments. Organic matter is an important, perhaps primary carrier of phosphorus to marine sediments. Due to the shorter water column in coastal waters, less respiration occurs prior to deposition. The larger flux of marine organic-P to margin sediments is accompanied by a larger direct terrigenous flux of particulate phosphorus (organic and inorganic), and higher sedimentation rates overall (e.g., Filippelli, 1997a,b). These factors combine to enhance retention of sedimentary phosphorus. During high sea-level stands the sedimentary phosphorus reservoir on continental margins expands, increasing the P-removal flux and therefore shortening the oceanic-P residence time (Ruttenberg, 1993).

Terrigenous-dominated shelf and slope (hemipelagic) sediments and abyssal (pelagic) sediments have distinct P-distributions. While both are dominated by authigenic Ca-P (P_{auth} : mostly authigenic apatite), this reservoir comprises a larger fraction of total phosphorus in pelagic sediments. The remaining phosphorus in hemipelagic sediments is partitioned between ferric iron bound-P (P_{Fe} : mostly oxyhydroxides), detrital apatite (P_{detr}), and organic-P (P_{org}); in pelagic sediments detrital apatite is unimportant, most likely due to limited transport of this heavy mineral beyond the near-shore. Certain coastal environments characterized by extremely high, upwelling-driven biological productivity and low terrigenous input are enriched in authigenic apatite; these are proto-phosphorite deposits (see Section 8.13.3.3.2 for further discussion). A unique process contributing to the pelagic sedimentary Fe-P reservoir is sorptive removal of phosphate onto ferric oxyhydroxides in mid-ocean ridge (MOR) hydrothermal systems (e.g., Wheat *et al.*, 1996; see Section 8.13.3.3.2).

Mobilization of sedimentary phosphorus by microbial activity during diagenesis causes dissolved phosphate buildup in sediment pore waters, promoting benthic efflux of phosphate to bottom waters or incorporation in secondary authigenic minerals. The combined benthic flux from coastal (sF_{cbf}) and abyssal (sF_{abf}) sediments is estimated to exceed the total riverine-P flux ($F_{24(d+p)}$) to the ocean. Reprecipitation of diagenetically mobilized phosphorus in secondary phases significantly enhances phosphorus burial efficiency, impeding return of phosphate to the water column (see Section 8.13.3.3.2). Both processes impact the

marine phosphorus cycle by affecting the primary productivity potential of surface waters.

8.13.3 PHOSPHORUS BIOGEOCHEMISTRY AND CYCLING: CURRENT RESEARCH

Many compelling lines of research are being pursued that seek to understand the biogeochemical controls on cycling of the essential nutrient, phosphorus, in terrestrial and aquatic systems; the research field is broad and deep. Limited space dictates that the summary of research presented in this chapter cannot be comprehensive. The more lengthy section on marine systems reflects the research bias of the author, and is not meant to convey any hierarchy of importance of marine research over terrestrial soil or freshwater studies. In fact, it can be argued from the standpoint of societal relevance that studies on terrestrial systems have higher significance, because anthropogenic impacts on terrestrial environments historically have been more severe. This is unfortunately changing, however, as the impact of humans on the terrestrial environment is bleeding over into the coastal ocean (e.g., Mackenzie *et al.*, 2002; Rabalais *et al.*, 1996; and references therein).

8.13.3.1 Phosphorus Cycling in Terrestrial Ecosystems and Soils

The process of sorptive binding of phosphate by iron (Fe)- and aluminum (Al)-oxide and oxyhydroxide phases is of enormous importance in terrestrial ecosystems, and has been extensively studied in soil science. Its importance lies in the fact that phosphorus can be a limiting nutrient in terrestrial ecosystems, and sorptive removal of natural or fertilizer phosphorus can impact the health and production level of crops and forests (e.g., Barrow, 1983; Guzman *et al.*, 1994; Frossard *et al.*, 1995). Unlike the Al-oxides/oxyhydroxides, Fe-oxides/oxyhydroxides are subject to reductive dissolution under anoxic conditions, and thus redox conditions can play an important role in soil P-bioavailability (e.g., Miller *et al.*, 2001). Fe- and Al-complexes with organic matter also can be important sinks for phosphate, as can clays, but the latter are less efficient scavengers of phosphate than the oxyhydroxides. Mineralogy and morphology of oxyhydroxides also exert control on relative efficiency of P-sorption; e.g., goethite is a more efficient substrate for P-sorption than is hematite (Torrent *et al.*, 1990; Filho and Torrent, 1993). Dissolved organic phosphorus compounds can also be sorptively removed from soil solution by various solid-phase components, including clays, oxides,

and oxyhydroxides (see Frossard *et al.* (1995) for a review of soil reactions involving phosphorus).

One unique ecosystem that has yielded an unparalleled natural laboratory for the study of soil and terrestrial ecosystem development in general, and the evolution of phosphorus and other nutrient bioavailability in particular, is the Hawaiian Island chain in the central subtropical Pacific Ocean (Vitousek *et al.*, 1997). These volcanic islands all have a soil substrate of basaltic rock with an essentially identical initial chemistry, are similar in climate, and are arrayed along an age transect from young, active volcanoes in the southeast to the oldest islands in the northwest. This system thus offers the opportunity for contemporaneous study of soil and ecosystem development processes that have occurred on thousand-year timescales, by comparing soil chemistry, nutrient availability, and ecosystem development on each of the islands, which range in age from 0.3 kyr to 4,100 kyr (Vitousek *et al.*, 1997).

During chemical weathering of bedrock and soil formation, rock-derived plant nutrients such as phosphorus, calcium, magnesium, and potassium are leached from parent rock and soil and are eventually lost from the system, or in the case of phosphorus, residual phosphorus is both lost and converted to unavailable forms (Figure 2), resulting ultimately in phosphorus limitation of the ecosystem. In their study of the Hawaiian Islands, Chadwick *et al.* (1999) validate this classical model of soil development, and determine that phosphorus acts as the “master regulator” of biological productivity in the most weathered soils, in agreement with existing conceptual models for terrestrial biogeochemistry. They also illuminate interesting variations on this classical theme. For example, as the soil evolved from newly formed to extensively aged substrate, nutrient limitation of the ecosystem evolved as well, from a system initially co-limited by phosphorus and nitrogen (when rock-derived nutrients calcium, magnesium, and potassium are plentiful, there has not been adequate time for soil accumulation of atmospherically derived nitrogen, and phosphorus is in bio-unavailable forms), to intermediate soils where cation availability is lower but nitrogen and phosphorus are more plentiful, and finally to highly weathered soils where cations and P-bioavailability are low but there is plentiful nitrogen. By evaluating nutrient sources to these Hawaiian soils, Chadwick *et al.* (1999) determine that in end-stage soils, atmospheric sources of cations from seasalt aerosols and phosphorus from atmospheric dust deposition are the dominant nutrient sources. By the oldest site on the soil chronosequence, phosphorus provided by Asian dust is substantially larger than that provided by the parent

rock and, in the absence of this distal source of phosphorus, these ecosystems would be far more severely P-limited (Chadwick *et al.*, 1999).

8.13.3.2 Phosphorus Cycling in Terrestrial Aquatic Systems: Lakes, Rivers and Estuaries

8.13.3.2.1 Biogeochemistry and cycling of phosphorus in lakes

Owing to their finite boundaries, lakes provide a more tractable venue as natural laboratories for mechanistic studies than do the oceans, and have therefore been the site of many elegant and informative studies on mechanisms of phosphorus cycling in aquatic systems (e.g., Schindler, 1970; Hecky and Kilham, 1988). Several concepts and processes of current intense interest in oceanography were first defined and examined in lakes, including (i) redox-driven coupled Fe–P cycling and benthic phosphorus efflux from sediments (Einsele, 1936a,b; Mortimer, 1941, 1942; and more recently, Böstrom *et al.*, 1988); (ii) the potential for direct biological control of benthic phosphorus efflux or uptake driven by shifts in redox conditions (Carlton and Wetzel, 1988; Gächter and Meyer, 1993; Gunnars and Blomqvist, 1997); and (iii) critical assessment of analytically defined “orthophosphate” (also known as soluble reactive phosphorus, or SRP) concentrations, as opposed to “true orthophosphate” concentrations (Rigler, 1966, 1968; and more recently Hudson *et al.*, 2000; see below). Other aspects P-biogeochemistry of keen interest in current oceanographic research have previously been extensively studied in lakes, including (i) definitive demonstration of phosphorus limitation of photosynthetic primary productivity (Schindler, 1970; Hecky and Kilham, 1988; Tarapchak and Nawelajko, 1986; however, see review by Fisher *et al.* (1995) summarizing studies of N-limited, or nitrogen and phosphorus co-limited lakes), (ii) bioavailability and composition of dissolved organic phosphorus (DOP) (Herbes *et al.*, 1975; Lean and Nawelajko, 1976; and more recently Nanny and Minear, 1997); (iii) the development and use of sequential extraction methods for sedimentary P-speciation (e.g., Williams *et al.*, 1976; Böstrom and Petterson, 1982); and (iv) phosphate mineral authigenesis (e.g., Emerson, 1976; Emerson and Widmer, 1978; Williams *et al.*, 1976). Research on a number of these topics is summarized in the remainder of this section.

There is disagreement about the relative importance of an indirect versus a direct microbial role in benthic phosphate flux as triggered by changes in redox state of bottom waters and sediments. The classical view is that microbial reduction and re-oxidation/re-precipitation of

ferric oxyhydroxides controls P-release versus P-retention by sediments by virtue of the high sorption affinity of ferric oxyhydroxides for phosphate (Einsele, 1936, 1938; Mortimer, 1941, 1942); an indirect microbial effect on benthic P-flux. While this mechanism clearly is important (e.g., Gunnars and Blomqvist, 1997), it has been shown that bacteria in surficial sediments directly take up and release phosphate in response to changes in redox state (Carlton and Wetzel, 1988; Gächter and Meyer, 1993), presumably due to redox-triggered changes in physiology. The relative importance of these two pathways for phosphorus cycling at the sediment–water interface is unclear. Further, whether the relative importance of these two mechanisms is different in lacustrine versus marine systems (Gunnars and Blomqvist, 1997) is an important unresolved question.

In an effort to systematize differences in the absolute magnitude of benthic phosphate efflux in freshwater versus marine systems, Caraco *et al.* (1989) argue that more efficient benthic P-release occurs in lake relative to marine sediments as a direct consequence of the presence of higher sulfate in seawater, and that redox conditions exert secondary control. This argument is overly simplistic, however, because redox conditions control production of sulfide from sulfate, and it is the removal of ferrous iron from solution into insoluble ferrous sulfides that decouples the iron and phosphorus cycles (e.g., Golterman, 1995a,b,c; Rozen *et al.*, 2002). Thus, the presence of sulfate is a necessary but not sufficient criterion to account for differences in benthic P-cycling in marine versus freshwater systems; redox conditions are an equally crucial factor.

The importance of redox effects on coupled iron–phosphorus cycling in freshwater systems has been the subject of study in applied environmental science, where phosphate removal from eutrophic natural waters and wastewaters, by sorption onto Fe-oxyhydroxide phases, has been explored as a remediation measure. Phosphate also has a pronounced tendency to sorb onto Al-oxyhydroxides, and these phases have been used in remediation of phosphate overenriched aquatic systems, as well (e.g., Leckie and Stumm, 1970).

Recently, Hudson *et al.* (2000) reported the smallest phosphate concentrations to date for any aquatic system (27 pM) in a study using a new, steady-state bioassay technique for estimating orthophosphate concentrations. In phosphate-limited aquatic systems, accurate determination of orthophosphate is critical because it is the only form of phosphorus that can be directly assimilated by primary producers (e.g., Cembella *et al.*, 1984a,b). The standard phosphomolybdate blue method for phosphate determination falls short of this goal, and is widely thought to overestimate

“true” orthophosphate concentrations due to reagent-promoted hydrolysis of DOP (e.g., Bentzen and Taylor, 1991; Rigler, 1966, 1968; however, see Monaghan and Ruttenberg (1999)). The findings of Hudson *et al.* (2000) suggest that “true” orthophosphate levels are 2–3 orders of magnitude lower than previously thought, equivalent to levels observed for micronutrients such as dissolved iron and zinc. Implications of this study include the possibility of diffusion-limited phosphate uptake, a situation favoring small organisms with large surface-to-volume ratios. This would further imply that bacteria may be net sinks for phosphate, rather than efficient remineralizers, as is the commonly held view, and may mean that phytoplankton have to adopt other competitive P-uptake strategies such as utilization of DOP (Karl, 2000). In another analytical development, Field and Sherrell (2003) have recently directly quantified the lowest ever measured concentrations of total dissolved phosphorus (and a number of other trace elements) in Lake Superior using a new ICP-MS method. Their method is unable to distinguish orthophosphate from other phosphorus forms, however, without application of prior separation techniques.

Alkaline phosphatase (APase) has been widely used in lake studies to demonstrate physiological phosphate stress, or P-limitation, of the bulk lake phytoplankton community (e.g., Healey and Hendzel, 1980; Cembella *et al.*, 1984a,b). A recent development in phytoplankton nutrient physiology research involves the use of a new, cell-specific labeling method for monitoring physiological phosphate-stress in phytoplankton and bacteria at the single-cell level (e.g., Carlsson and Caron, 2001; Rengefors *et al.*, 2001, 2003). In this method, when a phosphate group is cleaved from the ELF-97[®] (Molecular Probes) fluorescent substrate, the remaining molecule precipitates near the site of enzyme activity, thus fluorescently tagging cells that are expressing APase. The importance of this new method is that it monitors phytoplankton physiology at the single-cell level permitting, for example, the determination of differential phosphate stress among taxa, and even within taxa under the same environmental conditions (e.g., Rengefors *et al.*, 2003). This sort of cell-specific resolution is not possible with bulk APase assays, and the insights into phytoplankton nutrition made possible by the new ELF method have already revealed, and promise to continue to reveal previously inaccessible information on the nutrient physiological ecology of aquatic systems.

In summary, current research on P-cycling in lakes illustrates well that continued development and improvement of analytical methods is critical to addressing many long-standing unresolved

questions about biogeochemical P-cycling. This is true not just for lakes, but for other Earth surface environments, as well.

8.13.3.2.2 *Biogeochemistry and cycling of phosphorus in rivers and estuaries*

Rivers and streams are the major conduits of phosphorus transfer to the oceans and to many lakes (groundwaters are likely an important but unquantified dissolved phosphorus transport medium). Rivers themselves function as ecosystems, and biogeochemical processes that occur during riverine transport can modify the form of phosphorus *en route*, with consequences for its chemical reactivity and biological availability once it reaches the recipient water body. Because of its extreme particle reactivity, most phosphorus in rivers is associated with particulate matter, dominantly through sorption processes (Froelich, 1988). A substantial body of work has established that, in pristine rivers with high enough turbidity to minimize autotrophic biological phosphorus uptake, dissolved inorganic phosphorus (DIP) levels are set by sorption equilibrium with suspended sediments; this controlling mechanism is known as the phosphate buffer mechanism (see Froelich (1988) and Fox (1993) for a summary of research on this topic). Through controlled laboratory experiments monitoring P-uptake and release from synthetic ferric oxyhydroxides and natural riverine suspended sediments, under a range of riverine and estuarine conditions, Fox (1989, 1993) has more explicitly described the P-buffering mechanism as a thermodynamic equilibrium between DIP and a solid-solution of ferric phosphate-hydroxide in suspended colloids and sediments. This mechanism appears to be valid for a wide number of turbid rivers with low calcium levels, including the world's three largest rivers: the Amazon, Zaire, and Orinoco (Fox, 1993), suggesting a globally significant mechanism. In calcium-rich rivers such as the Mississippi, in contrast, DIP solubility appears to be controlled by equilibrium with a calcium phosphate mineral (Fox *et al.*, 1985, 1987). The impetus for investigating the P-buffering phenomenon has been the recognition that (i) phosphate buffering by suspended river sediments can maintain immediately bioavailable DIP at near-constant levels in rivers, streams, and estuaries; (ii) suspended sediments can act as a large source of potentially bioavailable phosphorus; and (iii) P-sorption onto soil and suspended sediments can effectively sequester pollutive-P (e.g., derived from fertilizer, waste water, etc.) in forms that are not immediately bioavailable, thereby reducing the effect of excess P-loading into terrestrial and coastal aquatic ecosystems.

The first comprehensive, systematic analysis of phosphorus transport by the world's rivers was compiled by Meybeck (1982). In this compilation, DIP, dissolved organic phosphorus (DOP), and particulate inorganic and organic phosphorus forms are separately reported for a wide range of river systems, recognizing that these different forms have different reactivities both geochemically and biologically. More recent global riverine-P flux estimates include Froelich *et al.* (1982), GESAMP (1987), Howarth *et al.* (1995), Colman and Holland (2000) and Smith *et al.* (2003). These compilations usually quantify phosphate concentrations and fluxes separately for pre-agricultural (pristine, or natural) and modern rivers.

An important use of global river flux estimates is in construction of element budgets for the oceans. Rivers are by far the dominant phosphorus source to the ocean (Table 2), and the oceanic phosphorus budget has been formulated by balancing riverine inputs against phosphorus burial with sediments by numerous groups (e.g., Froelich *et al.*, 1982; Colman and Holland, 2000; Compton *et al.*, 2000; Table 3, this chapter). An important factor in evaluating riverine P-input to the ocean, from the standpoint of accurately quantifying bioavailable-P input and balancing the marine phosphorus budget, is that some fraction of river suspended sediment releases its phosphorus to seawater. The magnitude of this "releasable-P" has been estimated as anywhere from 25% to 45% of the riverine suspended sediment flux (see Table 2, note (f), and Table 3). Detailed P-speciation studies in two major world rivers, the Amazon (Berner and Rao, 1994) and the Mississippi (Ruttenberg and Canfield, 1994), indicate that the phases responsible for riverine suspended sediment P-release in the coastal ocean are ferric oxyhydroxide associated phosphorus (see also Chase and Sayles, 1980) and particulate organic phosphorus. Important unanswered questions remain, including:

(i) To what extent are the Mississippi and Amazon representative of other rivers regarding the magnitude of P-release? Although these are globally significant rivers in terms of dissolved inputs, they do not have the high sediment yields of rivers in mountainous tropical regions (Milliman and Syvitski, 1992), for which there is scant phosphorus data.

(ii) To what extent are the Mississippi and Amazon representative of other rivers regarding the phases responsible for P-release? For example, within the Chesapeake Bay estuary, organic phosphorus does not appear to be an important source of P-release (Conley *et al.*, 1995). Until P-speciation data exists for more coupled river/shelf systems, it is not possible to evaluate the relative importance of different forms of

particulate-P as sources of bioavailable-P to the ocean.

(iii) What is the locus of and mechanisms for P-release from these (or other) phases at the continent-ocean interface? In particular, what are the relative importance of desorption from suspended sediments in the water column versus diagenetic remobilization in and release from benthic sediments?

(iv) At what point along the riverine/estuarine/marine salinity trajectory does P-release occur?

As the interface between rivers and the coastal ocean, estuaries are important sites of biogeochemical modification of phosphorus, as noted above (see also Section 8.13.2.2). Although not strictly terrestrial, the geography of many estuaries is often such that it is difficult to draw a clear boundary delineating where the terrestrial zone ends, and the oceanic zone begins. The nature of estuarine P-transformations has been a topic of interest since the 1950s, due to the importance of riverine transport in the global phosphorus cycle, and more recently because of recognition that human activity impacts the health of coastal zones. Recently published studies focused on resolving possible mechanisms of estuarine P-transformations, their locus of occurrence, and projected impacts on the adjacent and/or global ocean include studies on the Amazon shelf (DeMaster and Aller, 2001), Chesapeake Bay (Conley *et al.*, 1995); the northern Gulf of Mexico (Shiller, 1993; Rabalais *et al.*, 1996); and the estuaries fringing the North Atlantic Ocean (Nixon *et al.*, 1996; Galloway *et al.*, 1996; Howarth *et al.*, 1996); these recently published studies are a rich source of references to earlier work.

Elevated input of phosphorus and other nutrients via rivers to lakes and the coastal ocean has resulted in “cultural eutrophication” in many water bodies, a process that can lead to excessive accumulation of autotrophic (e.g., algal, macrophyte) biomass and ecosystem shifts to undesirable algal species. When excess algal biomass accumulates in bottom sediments, it stimulates heterotrophic activity that consumes oxygen, sometimes leading to development of anoxic sediments and bottom waters, with adverse effects for higher trophic levels (see discussions in Fisher *et al.*, 1995; Melack, 1995; Howarth *et al.*, 1995; Caraco, 1995; Nixon, 1995; Rabalais *et al.*, 1996; Richardson and Jørgensen, 1996). Recognizing the vulnerability of natural water systems to anthropogenic nutrient over-enrichment, and that integration of high-quality scientific data is required to formulate successful remediation strategies, a variety of national and international groups have banded together at various times to synthesize data from regional and/or global studies to provide a sound basis for management of aquatic resources (e.g., see summary of such efforts in Fisher *et al.*, 1995).

One recent example is “The Land Ocean Interactions in the Coastal Zone (LOICZ) Project,” a core project of the International Geosphere–Biosphere Program (IGBP), whose stated goals include a determination of nutrient fluxes between land and sea (with emphasis on carbon, phosphorus, and nitrogen), and an assessment of how coastal systems respond to varying terrestrial inputs of nutrients (Gordon *et al.*, 1996; Smith, 2001).

8.13.3.3 Biogeochemistry and Cycling of Phosphorus in the Modern Ocean

Areas of active research on the modern oceanic phosphorus cycle range from inquiries into the molecular composition of the dissolved organic phosphorus pool, to determinations of the global scale and distribution of authigenic phosphate minerals, to the perpetually plaguing question of whether phosphorus limits marine primary productivity and, if so, on what time and space scales. The next series of sections summarize first, an historic overview of the way in which our understanding of the oceanic phosphorus cycle has evolved over the past two decades. Next, recent and ongoing work on some of the most intriguing questions about the character and functioning of the oceanic phosphorus cycle are summarized.

8.13.3.3.1 Historical perspective: the marine phosphorus budget

The current vision of the marine phosphorus cycle differs substantially from that which prevailed as of the early 1980s. These changes have been driven by methodological developments, which have made new observations possible, as well as by challenges made to accepted paradigms as new studies have worked to reconcile new data with old, and sometimes entrenched, views.

The first comprehensive global marine phosphorus budget took the approach of quantifying phosphorus removal from the ocean by characterizing P burial rates in different depositional environments (Froelich *et al.*, 1982). These researchers took the important approach of separately quantifying P-burial rates for different depositional environments, and different sediment types, recognizing that the processes dominating in different environments would be distinct, and therefore subject to different controlling factors. This early incarnation of the marine phosphorus budget focused almost exclusively on the deep sea; the only ocean margin data included were from areas characterized by upwelling circulation and phosphorite formation, as the latter were recognized as hot-spots for phosphorus burial.

Notably, upwelling margins represent only 2% of the total marginal area of the ocean (Ganeshram *et al.*, 2002; Berner, 1982).

The emphasis on the pelagic realm was the result of the prevailing bias at the time, in both research and funding, toward blue water oceanography, whereas continental margins received far less research attention. The pelagic budget described by Froelich *et al.* (1982) was viewed as self-consistent, because the P-removal flux with sediments was balanced by the dissolved phosphate input flux with rivers, with a residence time of 80 kyr, similar to the canonical value of 100 kyr, the accepted residence time estimate at that time (Broecker and Peng, 1982).

Adopting the budgetary model of Froelich *et al.* (1982), Ruttenger (1993) presented a revised budget, this time taking into account the importance of continental margins, *in toto*, in the global marine P-cycle. Inclusion of the margins was motivated by a growing recognition of continental margins as extremely important depocenters for organic matter (Berner, 1982), and the knowledge that organic matter is one of the most, if not the most important vector for delivery of phosphorus to the seabed. An additional motivator for inclusion of continental margins was the recognition that the early diagenetic regime in organic-matter-rich margin sediments of all types, and not exclusively those underlying upwelling regimes, make these depositional environments likely places for authigenic carbonate fluorapatite (CFA) formation.

Identification of CFA in nonupwelling environments required the use of new, and indirect methods of detection, because dilution of this authigenic phase by the large burden of terrigenous material in many continental margin settings makes identification by direct methods, such as XRD, impossible. Ruttenger (1992) adapted existing methods for sequential extraction of phosphorus and trace metals from a variety of disciplines, including soil science, limnology, and marine geochemistry, resulting in the SEDEX method, which is able to separately quantify CFA. Application of a coupled SEDEX–pore water approach to continental margin sediments revealed that formation of authigenic CFA is not restricted to margin environments characterized by upwelling (Ruttenger and Berner, 1993, and others, see Section 8.13.3.3.2). Inclusion of continental margins in the global marine phosphorus budget increased the P-removal flux by 2–6 times (depending upon which burial flux estimates are used), due to high rates of burial in ocean margin sediments of organic phosphorus, authigenic CFA, and iron-bound phosphorus, the latter particularly

important in deltaic marginal environments (Table 3; Ruttenger, 1993).

More recent studies have further refined the estimated burial fluxes of phosphorus in the global marine phosphorus budget (Table 4), including better estimates of P-removal with iron oxyhydroxides at MORs (Wheat *et al.*, 1996), inclusion of burial fluxes for authigenic rare earth element- and thorium-phosphates (Rasmussen, 2000), phosphates buried in association with hydroxyapatite from fish bones, scales, and teeth (using a modified SEDEX method to separately quantify hydroxyapatite as distinct from CFA: Schenau *et al.*, 2000); and taking into account the return benthic flux of phosphate out of sediments (Colman and Holland, 2000). These and other studies (Compton *et al.*, 2000; Filippelli and Delaney, 1996) concur with Ruttenger (1993) that the earlier pelagic-focused budget of Froelich *et al.* (1982) underestimated global ocean P-burial fluxes, and therefore overestimated P-residence times (Table 3).

The higher P-burial rate estimates that these diverse groups have converged upon set up an imbalance in the global marine phosphorus budget when contrasted with the riverine dissolved P-input rate. This imbalance can be reconciled if some fraction of the phosphorus associated with riverine particulate matter is solubilized upon entry into the ocean (Table 2). Estimates of the quantity of phosphorus that might be liberated upon delivery from rivers to the oceans, or “releasable-P,” have been made in several studies (Ruttenger, 1993; Colman and Holland, 2000; Ruttenger and Canfield, 1994; Berner and Rao, 1994; Compton *et al.*, 2000; Howarth *et al.*, 1995; Ramirez and Rose, 1992; Froelich, 1988). Estimates made on the basis of P-inputs that include this “releasable” riverine particulate-P yield residence times that fall within the range of residence time estimates derived from P-burial fluxes (Table 3). Despite the large uncertainties associated with these numbers, as evidenced by the maximum and minimum values derived from both input and removal fluxes (Table 3), these updated residence times are all significantly shorter than the canonical value of 100 kyr. Residence times on the order of 10–17 kyr make feasible a role for phosphorus in perturbations of the ocean–atmosphere CO₂ reservoir on the timescale of glacial–interglacial climate change.

8.13.3.3.2 Diagenesis and burial of phosphorus in marine sediments

The sources of particulate phosphorus to the seabed include detrital inorganic and organic material transported by rivers to the ocean, biogenic material produced in the marine water column that sinks to the seabed, and atmospheric

Table 4 Geochemical partitioning of reactive-P burial fluxes.

| <i>Phosphorus reservoir</i> | <i>Phosphorus burial flux</i> (10^{10} mol yr ⁻¹) | <i>Method of determination</i> | |
|--|---|---|---|
| Organic-P | 1.1 | Delaney, 1998 (calculated from C _{org} burial rate and P _{org} /C _{org} ratios) | |
| | 1.5 | Froelich <i>et al.</i> , 1982 (calculated from C _{org} burial rate and P _{org} /C _{org} ratios) | |
| | 1.6 | Froelich, 1984 (calculated from C _{org} burial rate and P _{org} /C _{org} ratios) | |
| | 2.0 | Mach <i>et al.</i> , 1987 (calculated from C _{org} burial rate and P _{org} /C _{org} ratios) | |
| | 4.1 | Ruttenberg, 1993 (measured P _{org} via SEDEX method and estimated sediment delivery flux to the oceans) <i>Comments:</i> Variability in first four estimates results from different C _{org} burial fluxes and different P _{org} /C _{org} ratios chosen for estimated P _{org} burial fluxes (see Delaney, 1998 for summary). | |
| Authigenic CFA, Biogenic HAP, CaCO ₃ -P | 0.4 | Froelich <i>et al.</i> , 1982, 1988 (based on diagenetic modeling of sediment pore water) | |
| | 8.0 | Filippelli and Delaney, 1996 (assuming 80–90% of P _{total} measured via SEDEX method is P _{CFA} combined with P _{total} accumulation rates) | |
| | 9.1 (2.2) | Ruttenberg, 1993 (measured P _{CFA} via SEDEX method and estimated sediment delivery flux to the oceans; value in parentheses is minimum estimate, see comments) <i>Comments:</i> Froelich <i>et al.</i> estimates are for upwelling, classical phosphogenic provinces only. Ruttenberg's (1993) maximum estimate assumes all phosphorus measured in step III of the SEDEX method is truly authigenic. The minimum estimate assumes only the portion observed to increase above the concentration in the shallowest sediment interval is truly authigenic, accounting for the possibility that there may be a nonauthigenic background component to this reservoir (see Ruttenberg and Berner (1993) for an expanded discussion). HAP = hydroxyapatite (fish bones, teeth, scales). | |
| Ferric iron-bound P: Hydrothermal MOR Processes: | High-temperature ridge axis | 0.01 | Wheat <i>et al.</i> (1996) |
| | Low-temperature ridge flank | 0.65 | Wheat <i>et al.</i> (1996) basalt seawater reactions during convective circulation of seawater in sediments and crust of flanks of MORs |
| Hydrothermal plume scavenging | 0.77 | Wheat <i>et al.</i> (1996); Feeley <i>et al.</i> (1994) | |
| Total hydrothermal | 1.43 | | |
| Non-hydrothermal scavenging onto Fe-oxyhydroxides: | 1.5 | Froelich <i>et al.</i> , 1982 (in the Froelich <i>et al.</i> (1982) study, this quantity was attributed to burial with CaCO ₃ , determined by dissolving foram and coccolith tests from deep-sea cores. The work of Sherwood <i>et al.</i> (1987) and Palmer (1985) demonstrated conclusively that phosphorus associated with CaCO ₃ tests in the deep sea is nearly all associated with Fe-oxyhydroxide coatings on the tests. This quantity is therefore more accurately attributable to phosphorus burial with reactive Fe-oxyhydroxide phases (see also Ruttenberg, 1993) | |
| | 4.0 (0.4) | Ruttenberg, 1993 (measured P _{Fe} via SEDEX method and estimated sediment delivery flux to the oceans; value in parentheses is minimum estimate, see comments) | |

(continued)

Table 4 (continued).

| <i>Phosphorus reservoir</i> | <i>Phosphorus burial flux</i> (10^{10} mol yr ⁻¹) | <i>Method of determination</i> |
|--|---|--|
| Loosely sorbed P | 1.3 | <i>Comments:</i> Ruttenberg's (1993) maximum estimate assumes all phosphorus measured in step II of the SEDEX method is truly reactive-P. The bulk of the phosphorus reported in Ruttenberg (1993) was observed in deltaic sediments, however, and the possibility exists that some portion of this reservoir is detrital, and therefore does not represent phosphorus removed from seawater. Thus, the minimum estimate assumes that all of the deltaic P _{Fe} is detrital (this is an extreme, and likely unrealistic minimum end-member) Ruttenberg, 1993 (measured P _{exchg} via SEDEX method and estimated sediment delivery flux to the oceans) |
| Calcium carbonate | <0.009 | Delaney, 1998 (calculated from Holocene CaCO ₃ burial flux and maximum foraminiferal CaCO ₃ -P content from Palmer, 1985) <i>Comments:</i> Any phosphorus associated with CaCO ₃ tests, not surface metal oxyhydroxide coatings, is included in the quantity measured by step III of the SEDEX method; this estimate serves as a measure of the fraction of the step III, or the burial flux of authigenic apatite + biogenic apatite + CaCO ₃ , that can be accounted for by burial of CaCO ₃ . |
| REE phosphates and aluminum-phosphates | 6.56 | Rasmussen, 2000 (determined for ancient marine sandstones via microscopy, where sedimentary textures are the primary evidence used to argue that they are authigenic, and therefore representative of a reactive-P burial flux). <i>Comments:</i> These phases have yet to be observed in modern marine sediments, and their role as reactive phosphorus sinks in the ocean has yet to be verified. Verification of authigenic REE-P and Al-P formation in the modern ocean would strengthen arguments for the authigenic nature of these phases in ancient sediments. |

After Ruttenberg (1993), Delaney (1998), and Compton *et al.* (2000).

dust that becomes entrained with sinking particulate material and is thus transported to the seabed. Once at the sediment–water interface, refractory phosphorus phases, such as detrital apatites and other P-containing refractory crystalline minerals, are simply passively buried. Particulate phases that are reactive in the early diagenetic environment are subject to a number of biogeochemical processes that affect the extent to which they are retained in the sediment, and the form in which they are ultimately buried and become part of the sedimentary record. These processes include microbial breakdown of organic phosphorus and production of dissolved inorganic and organic phosphorus, uptake of phosphate via sorption, uptake of phosphate during formation of secondary phosphate minerals (the so-called authigenic minerals, because they form in place), and benthic efflux of dissolved phosphorus from sediments to bottom waters (Figure 3). Studies focusing on these and a number of other important early diagenetic processes are discussed in subsequent subsections.

Because phosphorus is an essential nutrient, processes controlling the extent of P-retention versus P-release from sediments are important

regulators of biological cycling and thus impact the workings of the global carbon cycle. This effect can be manifest on short timescales, where reactive particulate phases release phosphorus after deposition that is then returned to the water column where it is available for biological uptake. On longer, geologic timescales, the ultimate form in which phosphorus is buried will affect its susceptibility to weathering once it is uplifted into the weathering regime, and therefore its propensity for being rendered bioavailable in the next tectonic cycle. These links between early diagenesis of phosphorus, global ocean biological productivity, and the global carbon cycle, have been the motivation for much recent work on the biogeochemistry of phosphorus in modern marine sediments.

Sedimentary organic phosphorus: composition and reactivity. Organic phosphorus (P_{org}) is the primary vector of phosphorus delivery to marine sediments, and constitutes an important fraction (~25–30%) of total phosphorus buried in marine sediments (Froelich *et al.*, 1982; Ruttenberg, 1993; Colman and Holland, 2000). Despite its importance to the total marine sedimentary phosphorus

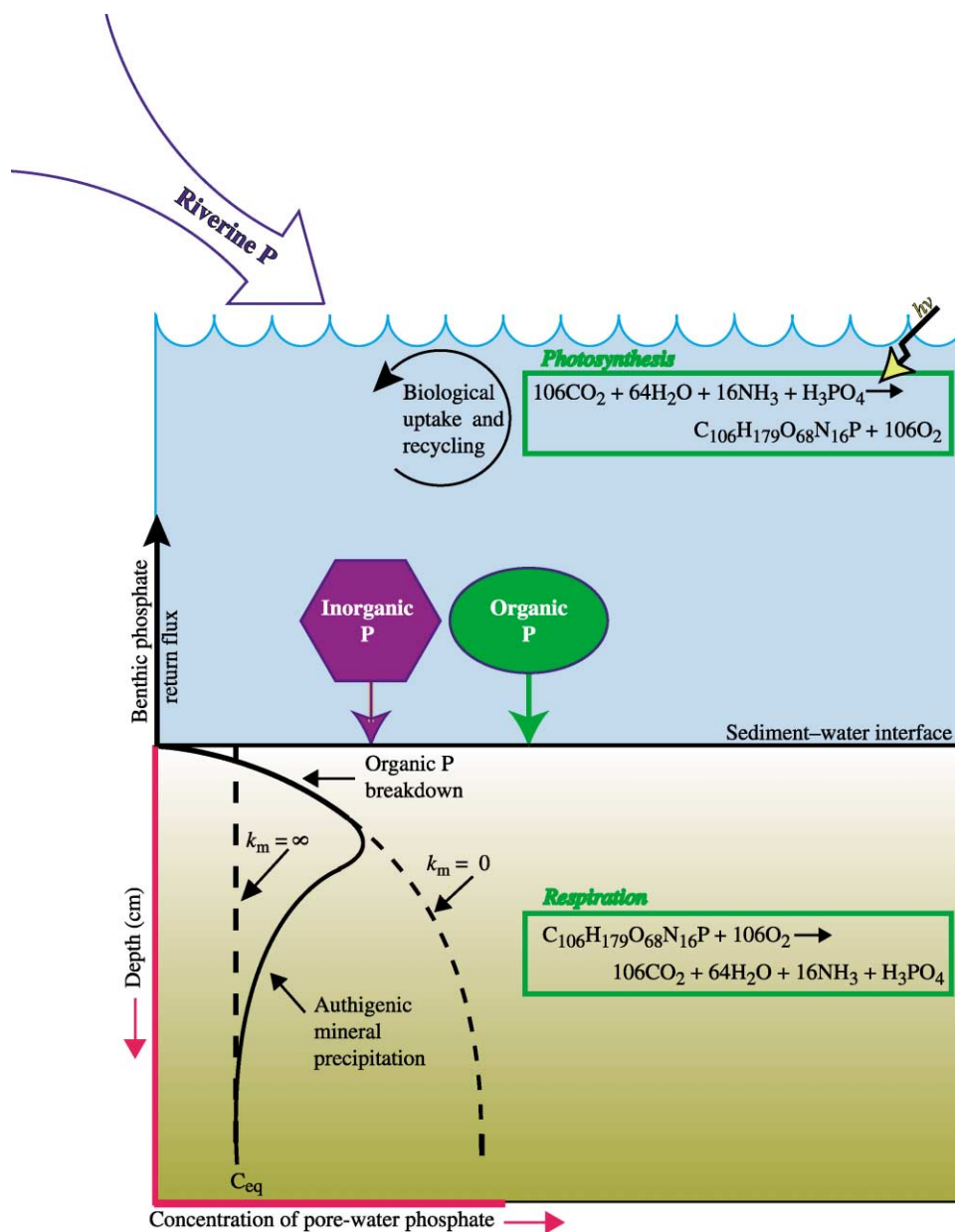


Figure 3 Processes important during early diagenetic transformations of phosphorus in marine sediments are illustrated. Sources of phosphorus to the sediment–water interface include allocthonous river-borne inorganic and organic phosphorus, and autocthonous, biogenic phosphorus formed through photosynthesis and subsequent food-web processes. Once delivered to the sediment–water interface, organic phosphorus is subject to breakdown via microbial respiration, a process often called “mineralization” because it transforms organic matter into its inorganic, “mineral” constituents, such as phosphate, nitrate, and carbon dioxide (dissolved organic phosphorus, nitrogen, and carbon, are also products of respiration, although these products are not shown). A representative equation for oxygenic respiration is given as an example, but a well-documented sequence of electron acceptors are utilized by microbial communities, typically in order of decreasing metabolic energy yield, to affect respiration (nitrate, oxides of iron and manganese, sulfate; however, for exceptions to this strict hierarchy of oxidants, see [Canfield, 1993](#); [Aller, 1994](#); [Hulth et al., 1999](#); [Anschutz et al., 2000](#)). All of these respiration reactions result in a buildup of phosphate and other metabolites in pore waters. Schematic of pore-water profiles for the general situation of steady-state phosphate diagenesis, with organic matter as the sole source of phosphate to pore waters, is after [Berner \(1980\)](#). (Another important source of phosphate to pore waters, not depicted in this cartoon, is release of sorbed phosphate from host Fe-oxyhydroxides when these phases are buried into suboxic and anoxic zones within the sediment (see text for discussion).) Once released to pore waters, phosphate can escape from sediments via diffusional transport, resuspension, or irrigation by benthos. An important process for retention of pore-water phosphate within sediments is secondary authigenic mineral formation. The dashed profiles illustrate phosphate profile shapes encountered when

inventory, advances in understanding the compositional make-up of sedimentary organic phosphorus have been fairly limited, due in large part to the analytical difficulties associated with characterizing its molecular forms. The principal analytical challenge is that only a small fraction of sedimentary organic phosphorus can be separated into individual organic phosphorus compounds for identification and analysis; the bulk of the pool (in most cases well over 90%) is intimately associated with high-molecular-weight (HMW) bulk organic matter (Laarkamp, 2000), and is inaccessible to most existing analytical methodologies.

One of the most intriguing, and persistent, questions concerning the marine sedimentary organic phosphorus reservoir is the following: Given that the ultimate source of organic phosphorus to marine sediments is the phosphorus biochemicals contained within plant and animal tissues, and that these biochemicals are high-energy compounds that presumably should be labile after the death of the organism, how is it that significant quantities of organic phosphorus persist in deeply buried (Filippelli and Delaney, 1996; Delaney and Anderson, 1997; Tamburini *et al.*, 2003) and even in ancient (Ingall *et al.*, 1993) marine sediments? What is the mechanism by which these compounds are preserved? Persistence of organic phosphorus in deeply buried and ancient marine sediments has been explained in a number of ways, including, (i) preferential preservation of inherently refractory organic phosphorus compounds such as phosphonates or inositol phosphates (Froelich *et al.*, 1982; Ingall and Van Cappellen, 1990; Suzumura and Kamatani, 1995), and (ii) presence of bacterial biomass or derivative compounds (Froelich *et al.*, 1982; Ingall and Van Cappellen, 1990; Ruttenger and Goñi, 1997a). Without insight into the composition of sedimentary P_{org} , it is not possible to conclusively determine controls on its relative reactivity or lability during early diagenesis, and thus to understand preservation mechanisms.

Most information about sedimentary organic phosphorus derives from studies focusing on the size of the total P_{org} pool and bulk organic C : P ratios in sediments (Filipek and Owen, 1981; Froelich *et al.*, 1982; Krom and Berner, 1981; Ingall and Van Cappellen, 1990; Ingall *et al.*, 1993; Morse and Cook, 1978; Reimers *et al.*, 1996; Ruttenger, 1993; Ruttenger and Goñi, 1997a,b; Anderson *et al.*, 2001) without examining

distribution among specific P_{org} compounds or compound classes. The size of the bulk P_{org} pool in marine sediments typically decreases with depth, indicating partial mineralization during early diagenesis (Krom and Berner, 1981; Morse and Cook, 1978; Filippelli and Delaney, 1996; Reimers *et al.*, 1996; Ruttenger and Berner, 1993; Slomp *et al.*, 1996a,b; Ruttenger and Goñi, 1997a; Shenau *et al.*, 2000; Filippelli, 2001; Van der Zee *et al.*, 2002; see also Figure 9(a), this chapter). Deeper in the sediments, mineralization of P_{org} slows to undetectable levels. The initial rapid mineralization of P_{org} is usually attributed to destruction of more labile components (Ingall and Van Cappellen, 1990; Krom and Berner, 1981), and by inference the deeply buried P_{org} is assumed to be more refractory. In some slow sediment accumulation rate sites such as in the deep sea, however, sedimentary P_{org} concentration profiles can be invariant with depth, implying that even P_{org} at the sediment water interface is refractory toward microbial mineralization (Ruttenger, 1990). Bulk P_{org} concentrations alone, however, do not provide a means for explicitly supporting these inferences. Key questions include: (i) What specific P_{org} compounds make up the “labile” portion of the P_{org} pool? (ii) What is the chemical composition of the preserved, presumably refractory, P_{org} fraction?

Less frequently, studies have been undertaken to quantify a limited number of compounds (e.g., ATP, DNA, phospholipids) within marine sediments (Crave *et al.*, 1986; Harvey *et al.*, 1986; White *et al.*, 1979). The relative rarity of the latter types of studies is in large part because they require substantially more work than studies of the bulk P_{org} pool. Furthermore, the aim of such studies is usually distinct from the goal of understanding the sedimentary P_{org} pool *in toto*. Rather, these studies typically seek to understand biomass distribution or microbial activity in sediments, for which these biochemicals may serve as proxies.

Suzumura and Kamatani (1995) pursued a study of the fate of inositol phosphates in sediments, another specific class of compounds that can be isolated and quantified, with the quite different aim of evaluating whether these terrestrial plant-derived P_{org} compounds might be refractory in the marine environment. Their results suggest that these compounds are minor constituents of total P_{org} in marine sediments, and that they are vulnerable to microbial breakdown during early

(i) organic matter breakdown is the dominant process, and there is no precipitation ($k_m = 0$: exponential increase of pore-water phosphate with increasing depth), and (ii) there is very rapid precipitation ($k_m = \text{infinity}$: vertical gradient at a concentration (C_{eq}) in equilibrium with the authigenic phase). The intermediate case is given in the solid curve, where a reversal of the initially exponentially increasing pore-water gradient is observed, indicating removal of phosphate from pore waters during phosphate mineral authigenesis.

diagenesis and do not persist to depth. Thus, these compounds do not provide an explanation for persistent preservation of P_{org} in marine sediments.

Although studies of specific P_{org} compounds such as these have expanded our understanding of the sedimentary P_{org} pool, their narrow focus on compounds which make up at most a few percent of the total P_{org} pool contribute little to our understanding of the forces driving bulk P_{org} trends in marine sediments.

Early work undertaken to examine the composition of the bulk sedimentary P_{org} pool separately quantified phosphorus associated with humic and fulvic acids in marine sediments (Nissenbaum, 1979). Results of this study suggested that phosphorus is preferentially mineralized during the diagenetic transition from fulvic to humic acid. However, because the distinction between organic and inorganic phosphorus in these fractions was not made, it is unclear whether the trends reported accurately reflect changes in P_{org} .

A decade after Nissenbaum's (1979) work, new advances in our understanding of the bulk sedimentary P_{org} pool began to be made with the application of phosphorus-31 nuclear magnetic resonance spectroscopy (^{31}P -NMR) to marine sediments. ^{31}P -NMR is currently the most promising tool for characterizing P_{org} in sediments. Application of ^{31}P -NMR to the insoluble "protokerogen" fraction of marine sediments has revealed the presence of phosphonates (Ingall *et al.*, 1990; Laarkamp, 2000; Ruttenberg and Laarkamp, 2000). Phosphonates were originally viewed as promising candidates for compounds that might make up the refractory sedimentary P_{org} pool because their structure (a direct carbon-phosphate bond) was thought to render them more stable than organic phosphates (Froelich *et al.*, 1982; Ingall *et al.*, 1990; Ingall and Van Cappellen, 1990). However, recent work using solution phase ^{31}P -NMR coupled with a new organic phosphorus sequential extraction method (Laarkamp, 2000) has shown that phosphonate esters are equally, if not more, vulnerable to microbial breakdown during early diagenesis than phosphate esters. Thus, the direct C-P bond in phosphonates does not appear to render these compounds more resistant to microbial respiration in marine sediments (Laarkamp, 2000; Ruttenberg and Laarkamp, 2000). The nature of the "refractory" organic phosphorus that escapes breakdown during early diagenesis, substantial quantities of which make it into the rock record, and can be quantified as P_{org} in ancient shales (Ingall *et al.*, 1993; Laarkamp, 2000), thus remains an open question.

Authigenic Carbonate Fluorapatite (CFA): Modern Phosphorites. Carbonate fluorapatite (CFA), or francolite, is the dominant phosphatic

mineral in phosphorite deposits. Phosphorites are marine sedimentary deposits containing greater than 5 wt.% and up to 40 wt.% P_2O_5 (McKelvey, 1967; Riggs, 1979; Cook, 1984); a lower threshold of 15–20% P_2O_5 is commonly cited (Bentor, 1980; Jarvis *et al.*, 1994). These high concentrations are in contrast to most sedimentary rocks and sea-floor sediments, which contain less than 0.3 wt.% P_2O_5 (0.13 wt.% P) (Riggs, 1979). The high phosphorus concentrations of phosphorites place them in the category of economic ore deposits, and they are actively mined for P used predominantly in fertilizer (e.g., Fisher *et al.*, 1995; Melack, 1995; and see Section 8.13.2.2.1).

CFA is a substituted form of fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$), with a variety of cations substituting for calcium, and anions substituting for both phosphate and fluoride, respectively. Apatites have an extremely accommodating crystal lattice, and their chemical composition takes on the characteristics of the precipitating fluid (McConnell, 1973; McClellan, 1980; Kolodny, 1981; Jarvis *et al.*, 1994). Marine authigenic CFA, which forms within marine sediments, thus incorporates aspects of the chemistry of the interstitial pore fluids of the sediment within which it forms. There have been numerous general chemical formulae proposed to capture the possible permutations of the chemical composition of marine authigenic CFA (e.g., Jahnke, 1992). A fairly comprehensive general formula has been proposed by Jarvis *et al.* (1994): $(\text{Ca}_{10-a-b} \text{Na}_a \text{Mg}_b (\text{PO}_4)_{6-x} (\text{CO}_3)_{x-y-z} (\text{CO}_3\text{F})_y (\text{SO}_4)_z \text{F}_2)$. The most important distinction between pure fluorapatite, typically formed by igneous processes, and CFA, is the presence of carbonate within the apatite crystal lattice. Disagreement exists about whether the carbonate substitutes for phosphate or for fluoride (LeGeros *et al.*, 1969; McConnell, 1973; McClellan, 1980; Kolodny, 1981), but regardless of its position within the lattice, its presence acts to distort the lattice and increase its solubility (LeGeros, 1965; LeGeros *et al.*, 1967; McConnell, 1973; McClellan, 1980; Jahnke, 1984). It is this difference in solubility that forms the basis for the ability to separately quantify CFA and detrital fluorapatite by the SEDEX method. Once out of the early diagenetic environment, with increasing age, and particularly upon metamorphism or uplift and exposure to subaerial weathering, CFA has a tendency to lose its marine-derived substituents and recrystallize to the thermodynamically more stable unsubstituted fluorapatite (Jarvis *et al.*, 1994; Lucas *et al.*, 1980; McArthur, 1980; McClellan, 1980).

Phosphorites are generally thought to be the result of postdepositional concentration of CFA from a primary sediment deposit, which contained more disseminated CFA, by secondary physical processes such as winnowing and reworking. The classical depositional environments in which

these deposits form have two main characteristics: high marine organic matter (and therefore P_{org}) flux to sediments and low detrital input. Such environments are found in the eastern margins of the oceans, where wind-driven upwelling of nutrient-rich deep waters sustains a highly productive biological community in surface waters, which in turn provides a rich source of organic matter, and thus organically bound phosphorus, to underlying sediments. The continents adjacent to margins characterized by wind-driven upwelling tend to be arid, such that transport of continental detrital material to the adjacent ocean by runoff is relatively low, minimizing potential dilution of authigenic CFA within the sediment column. These two factors predispose the sediments to formation and concentration of CFA at the high levels necessary for formation of a phosphorite deposit (Baturin, 1983; Cook and McElhinny, 1979; Bentor, 1980; Kolodny, 1981; Burnett *et al.*, 1983; Föllmi, 1995a,b). Other factors have been cited as potentially important for phosphorite formation (Table 5), but there is not consensus on many of these.

Interestingly, although archaic phosphorites had been well documented in the geologic record and on the seafloor since the mid-1800s (Bentor, 1980; Föllmi, 1995a,b), until recently it was widely held that phosphorites were not forming in the modern ocean (Kolodny, 1969; Kolodny and Kaplan, 1970). This lent a certain mystique to these ancient deposits, in that it was unclear how the oceans of the past might have differed from the present day ocean, such that deposition of these hugely concentrated phosphorus deposits was

favoured. This paradox was de-mystified in the 1970s, with the application of uranium-series dating to seafloor phosphorites in sediments from the Peru upwelling zone, which demonstrated that contemporary phosphorite formation was indeed occurring (Baturin *et al.*, 1972; Veeh *et al.*, 1973; Burnett, 1977; Burnett *et al.*, 1980). Later detailed studies of pore water and solid phase chemistry provided corroborating evidence for contemporary formation of CFA in these sediments (Froelich *et al.*, 1988; Glenn and Arthur, 1988). Burnett *et al.* (2000) have pursued a number of radiochemical studies of phosphorite nodules and crusts in order to document rates and modes of precipitation, and find growth rates of 2–9 mm kyr⁻¹ in response to downward diffusion of phosphate from pore-water phosphate maxima present just below the sediment–water interface. Postprecipitation winnowing causes re-exposure of the so-called phosphorite “proto-crusts” at the sediment surface, where erosion into the more common and widespread phosphatic hardgrounds, conglomerates, and nodules found in sediments of the Peru shelf occurs. Modern-day phosphorites are now also known to form on the Namibian shelf (Thompson *et al.*, 1984; Baturin, 2000, and references therein), in sediments adjacent to Baja California (Jahnke *et al.*, 1983; Schuffert *et al.*, 1994), on the Oman margin (Schenau and De Lange, 2000), and on the eastern Australian margin (Heggie *et al.*, 1990; O’Brien *et al.*, 1990).

In contemporary Peruvian, Baja Californian, and eastern Australian margin sediments, the confluence of pore-water gradients in phosphate and fluoride concentration with sedimentary phosphorite layers are consistent with active CFA formation, and careful work in these environments has provided insight into the process of modern-day phosphorite formation in these classical phosphorite environments. For example, Schuffert *et al.* (1994), working in sediments underlying the upwelling regime off the west coast of Baja California, Mexico, observed downward decreasing pore-water concentration gradients of both phosphate and fluoride, reflecting removal of these ions from pore water as they are incorporated into authigenic CFA (Figure 4). Coincidence of inflections in these pore-water gradients with the occurrence of XRD-identified CFA layers in the solid phase (stippled bands in Figure 4) is conclusive evidence for CFA formation in these sediments. In all but one core examined, the coupled pore-water and solid-phase data suggest contemporary formation of CFA in the uppermost one or two layers, while deeper layers reflect relict episodes of CFA formation, presumably that were active when these layers were located closer to the sediment–water interface (Schuffert *et al.*, 1994). As further confirmation of removal of phosphate from pore

Table 5 Summary of factors leading to phosphorite formation.

| Factor | Reference |
|---|------------------|
| Large supply of particulate organic matter | 1, 2, 3, 4, 5, 6 |
| Warm temperatures | 1, 2 |
| Associated with interglacials, high sea level | 1, 7 |
| High salinity | 2 |
| Elevated pH | 1, 2, 8 |
| Low accumulation rate of inorganic material | 2, 4 |
| Associated with extinctions, major evolutionary events | 3, 9 |
| Associated with the boundaries of the oxygen minimum zone | 1, 4 |
| High pore water calcium:magnesium ratio | 1, 10 |

After Jahnke *et al.* (1983).

References: (1) Burnett (1977); (2) Gulbrandsen (1969); (3) Piper and Codispoti (1975); (4) Manheim *et al.* (1975); (5) Baturin and Bezrukov (1979); (6) Van Cappellen and Berner (1988); (7) Riggs (1984); (8) Reimers *et al.* (1996); (9) Cook and Shergold (1984); (10) Van Cappellen and Berner (1991). See also Cook *et al.* (1990) for a succinct summary of models for phosphogenesis.

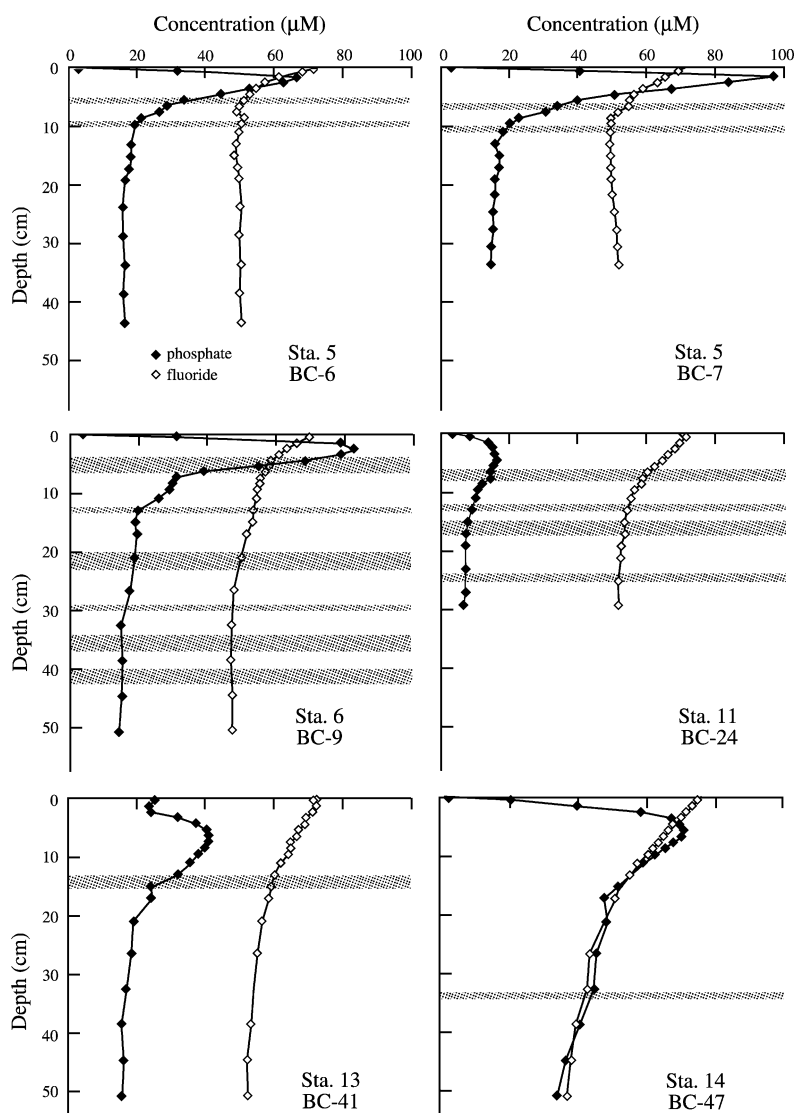


Figure 4 Pore-water profiles showing coupled removal of dissolved phosphate and fluoride from pore waters with depth in sediments, suggesting active growth of CFA in these Baja California sediments. Stippled bands indicate position and width of discrete phosphorite layers, as detected visually and confirmed by X-ray diffraction. Downward extent of concentration gradients indicates that CFA can precipitate simultaneously in two or more phosphorite layers (after Schuffert *et al.*, 1994).

water to form CFA, Schuffert *et al.* (1994) executed a stoichiometric nutrient regeneration model to predict pore-water phosphate profiles from pore-water ammonium and total alkalinity gradients, and contrasted these predicted profiles to the empirically observed phosphate profile (Figure 5). The results of this model reveal that the subsurface maximum in phosphate, which is unpredicted by the stoichiometric nutrient regeneration model, must be the result of input from some other process than “normal” organic matter decay, a finding highlighted for this region previously by Van Cappellen and Berner (1988). One likely explanation proposed by Schuffert *et al.* (1994) is that it is linked to the diagenetic redox

cycling of iron oxyhydroxides, as has also been suggested in other studies (Shaffer, 1986; Heggie *et al.*, 1990; Sundby *et al.*, 1992; Jarvis *et al.*, 1994; Slomp *et al.*, 1996; see also Section 8.13.3.2). A schematic of the coupled cycling of iron and phosphorus, and the proposed link to CFA (or francolite) formation during early diagenesis, shows the sequence of events and their distribution relative to different redox zones within a sediment (Figure 6). Fluoride is also scavenged by *in situ* formed iron oxyhydroxides (Ruttenberg and Canfield, 1988), and thus the iron redox cycle in sediments acts as a concentrating mechanism for these CFA substituents which, when released to pore water upon reduction of

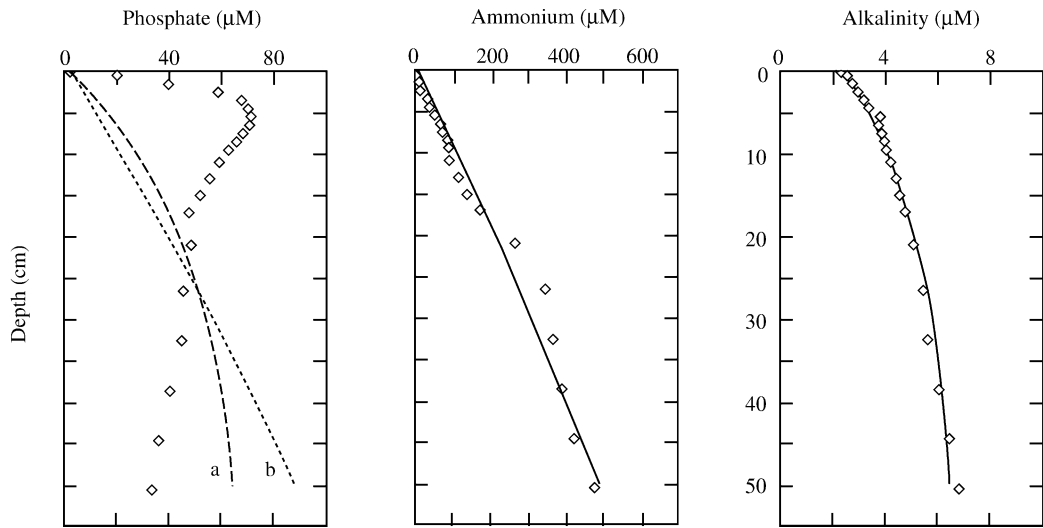


Figure 5 Measured and model-predicted pore-water profiles of dissolved nutrients for one of the Baja California cores shown in Figure 4: Station 14 (BC-47), after Schuffert *et al.*, 1994. Data appear as filled diamonds. Solid curves for alkalinity and ammonium represent empirical fits generated from a steady-state diagenetic model for stoichiometric nutrient regeneration from microbial breakdown of organic matter (see Schuffert *et al.*, 1994, for details). Dashed curves for pore-water phosphate represent model predictions for phosphate concentration gradients derived from the curve fits shown for the (a) alkalinity and (b) ammonium data, assuming organic matter is the sole source of phosphate, and no authigenic CFA formation. The overprediction of pore-water phosphate at depth suggests that the model requires a removal term, e.g., authigenic CFA formation. The underprediction at the surface implies another source of phosphorus to pore waters in addition to organic matter decay (see text for discussion).

the iron oxyhydroxide substrate at depth, provide a spike of phosphate and fluoride which may be instrumental in triggering CFA formation (Heggie *et al.*, 1990; Ruttenger and Berner, 1993; Jarvis *et al.*, 1994; Reimers *et al.*, 1996; Slomp *et al.*, 1996a).

The over-prediction of pore-water phosphate at depth (Figure 5) is likely due to phosphate removal of organic-matter-derived phosphate into authigenic CFA, a finding that is in accordance with other, similar applications of stoichiometric nutrient regeneration models to document the process of authigenic CFA formation (Ruttenger and Berner, 1993; Slomp *et al.*, 1996a). A further conclusion of the modeling work on pore-water data was an estimate of authigenic CFA precipitation rates for this site, which agree well with rates estimated for the contemporary Peruvian margin phosphorites (Froelich *et al.*, 1988), and for several large phosphorites of the recent geologic past, now exposed on land (Froelich *et al.*, 1988; Filippelli and Delaney, 1992).

Disseminated Authigenic Carbonate Fluorapatite. Once thought to be a phase that formed only in limited areas characterized by specific and stringent depositional environmental conditions (Table 5; see previous section), evidence accumulated during the 1990s strongly suggests that formation of authigenic CFA is a widespread phenomenon in the oceans (Figure 7). As mentioned previously, in most continental

margin areas and in pelagic environments, detection of authigenic CFA against a large burden of detrital sediment cannot be accomplished through direct mineralogical analysis by XRD or SEM, the standard methods used for its detection and quantification in phosphorite and protophosphorite deposits (e.g., Schuffert *et al.*, 1990; Schuffert *et al.*, 1994; Baturin, 2000). Those studies during the 1990s that have documented CFA in nonphosphorite sediments have used the SEDEX method (Ruttenger, 1992), a sequential extraction method designed expressly to quantify CFA as distinct from detrital igneous and metamorphic apatites. The most robust of these studies have used pore-water profiles in combination with the SEDEX method, the so-called “coupled pore-water–SEDEX approach,” which allows the application of four diagnostic indicators of CFA formation (Ruttenger and Berner, 1993): (i) downward decreasing pore-water fluoride gradients, (ii) decoupled pore-water phosphate and ammonium gradients where, assuming stoichiometric nutrient regeneration in sediments, deficits in phosphate relative to ammonium indicate phosphate removal (see Figure 5), (iii) calculated saturation state of CFA, and (iv) identification of CFA in sediments via the SEDEX method. These diagnostic indicators, although indirect, are the only available tools for identifying authigenic CFA when it is diluted in sediments with a high burden of terrigenous detrital material.

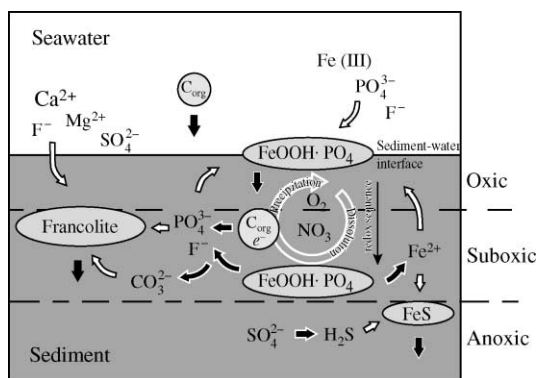


Figure 6 Schematic diagram of the coupled iron and phosphate cycles in during early diagenesis in marine sediments. Light gray ovals and circles represent solid phases, black arrows are solid-phase fluxes. White-outlined black arrows indicate reactions, white arrows are diffusion pathways. Ferric oxyhydroxides (FeOOH) precipitated in the water column and at the sediment–water interface scavenge phosphate (PO_4^{3-}) and some fluoride (F^-) from seawater. During burial and mixing, microbial respiration of organic matter utilizes a sequence of electron acceptors in order of decreasing thermodynamic advantage. Oxygen is used first, followed by nitrate and nitrite, manganese- and iron-oxyhydroxides, and sulfate. Phosphate is liberated to pore waters upon decomposition of organic matter, and reductive dissolution of FeOOH liberates Fe^{2+} , PO_4^{3-} , and F^- , resulting in increases in concentrations of these ions in pore waters (e.g., see phosphate profile in Figure 3 and model curves in Figure 4). If concentration levels are sufficient to exceed saturation with respect to authigenic CFA (denoted as francolite in figure), this phase will precipitate out of solution, sometimes first as a precursor phase that then recrystallizes to CFA proper. Excess phosphate diffuses up towards the sediment–water interface, where it is readsorbed by FeOOH. Ferrous iron (Fe^{2+}) diffuses both downwards to be precipitated with sulfide as FeS in the anoxic zone of sediments, and upwards to be re-oxidized in the oxic zone, where it is reprecipitated as FeOOH. The Fe-redox cycle provides an effective means of trapping phosphate in sediments, and can promote the precipitation of CFA (after Jarvis *et al.*, 1994).

The SEDEX method (Ruttenberg, 1992) is a multistep selective, sequential extraction method that separately quantifies five distinct sedimentary phosphorus reservoirs on the basis of their chemical reactivity to a sequence of solvents: (i) loosely sorbed, or exchangeable phosphorus, (ii) ferric-iron-bound phosphorus, (iii) authigenic carbonate fluorapatite, biogenic hydroxyapatite, plus CaCO_3 -bound phosphorus, (iv) detrital apatite, and (v) organic phosphorus (Figure 8). The method was standardized for application in marine sediments using analogues for marine phosphorus phases. There have been several modifications proposed to the method that have aimed to streamline the procedure (Anderson and Delaney, 2000; Slomp *et al.*, 1996a,b; Berner

and Rao, 1994; Ruttenberg and Ogawa, 2002), but the sequence of solvents in all of these remains fundamentally the same. Exceptions to the streamlining approach are Jensen *et al.* (1998), who expanded the SEDEX method by combining it with another sequential extraction method permitting separation of seven P-reservoirs, and Vink *et al.* (1997), who inserted an additional step between steps I and II of the SEDEX method to remove labile organic phosphorus using the surfactant sodium dodecyl sulfate (SDS). The SDS step was standardized in the same way that the original SEDEX method was standardized (Ruttenberg, 1992), and it appears that it is efficient and specific for labile organic phosphorus. The merit of this approach is that it separately quantifies labile organic phosphorus that might otherwise be lost in subsequent, more aggressive steps of the sequence. The potential benefits of these expanded methods must, however, be weighed against the burden of extending an already arduous analytical method.

The most salient feature of the SEDEX scheme is the ability to separately quantify authigenic CFA as distinct from detrital igneous and metamorphic apatite, as the former represents an active sink for phosphorus from the ocean, whereas the latter does not. Schenau and De Lange (2000) recently proposed adding a series of NH_4Cl extractions to the SEDEX method in order to separately quantify biogenic hydroxyapatite (fish bones, teeth, and scales), as distinct from authigenic apatite. This modification is important for studies wishing to quantify fish debris in sediments, but provides no additional information on removal of reactive phosphorus from the ocean, since the hydroxyapatite reservoir is quantified in step III of the original SEDEX scheme, along with CFA and CaCO_3 -P.

One of the most important outcomes of application of the SEDEX method in studies of early diagenesis of phosphorus in marine sediments has been identification of modern-day disseminated CFA formation in sediments from nonupwelling regimes (Figure 7). This finding is important because it requires a revision of thinking regarding the role of phosphogenesis and phosphorites in the oceans. That is, there is nothing glaringly unique about the classical phosphorite-forming environment with regard to its propensity for authigenic CFA formation; such conditions potentially exist anywhere that pore-water concentrations of constituent ions satisfy the thermodynamic condition of saturation or supersaturation with respect to CFA. Rather, the uniqueness of phosphorite forming environments has to do with secondary processes that act to concentrate CFA, and/or with low sedimentation rates, which minimize dilution of CFA. The finding of disseminated CFA in a wide range of

Distribution of disseminated CFA, recent and fossil phosphorites, and their relationship to upwelling areas

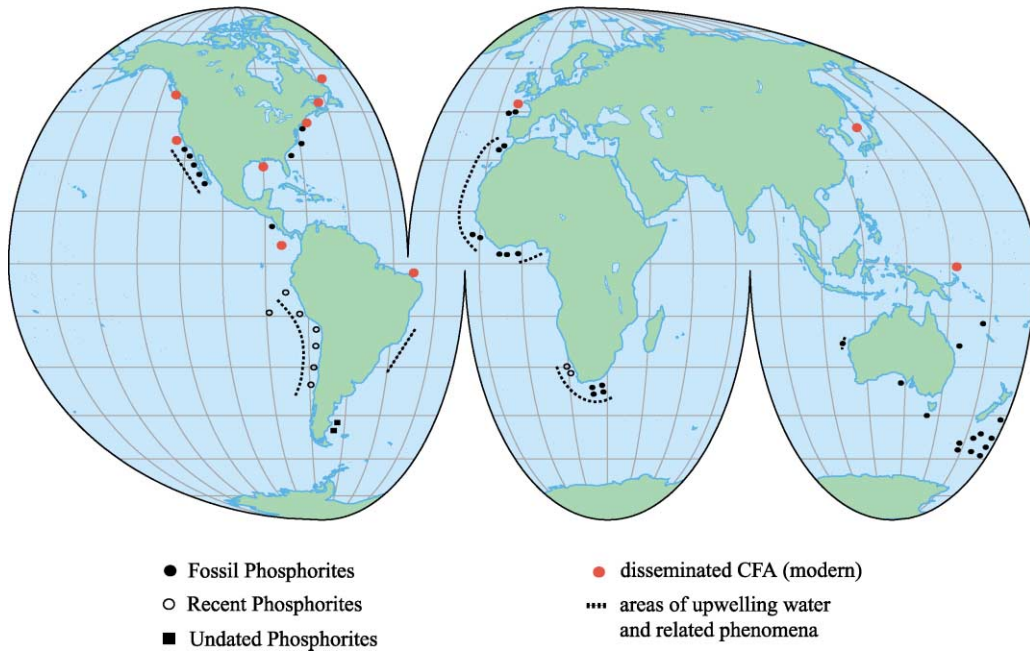


Figure 7 Locations of disseminated (nonphosphorite) authigenic CFA occurrence, as identified using the SEDEX method, as well as locations of fossil, recent, and undated phosphorites. Note that most phosphorites are located in continental margin areas characterized by upwelling, a process whereby nutrient-rich deep waters are advected to the surface causing high biological productivity and a resulting large flux of organic matter to underlying sediments. Sites of disseminated CFA, in contrast, are not restricted to these classical phosphorite-forming environments. Disseminated CFA data are from [Cha, 2002](#) (East Sea between Korea and Japan); [Delaney and Anderson, 1997](#) (Ceara Rise); [Filippelli, 2001](#) (Saanich Inlet); [Filippelli and Delaney, 1996](#) (eastern and western equatorial Pacific); [Kim *et al.*, 1999](#) and [Reimers *et al.*, 1996](#) (California Borderland Basins); [Louchouart *et al.*, 1997](#) (Gulf of St. Lawrence); [Lucotte *et al.*, 1994](#) (Labrador Sea); [Ruttenberg and Berner, 1993](#) (Long Island Sound and Gulf of Mexico); [Slomp *et al.*, 1996a](#) (North Atlantic continental platform; [Van der Zee *et al.*, 2002](#) (Iberian margin in the NE Atlantic). See text for more detailed discussion of selected studies. Figure is modified after [Kolodny \(1981\)](#), by addition of disseminated CFA locales; see [Kolodny \(1981\)](#) for discussion of phosphorite locales.

geographically distinct, nonclassical phosphorite-forming environments has an even more important ramification for the global marine phosphorus cycle, however, in that CFA acts as a permanent sink for reactive phosphorus from the oceans. Thus, the discovery that formation of this phase is not restricted to upwelling environments substantially increases burial rate estimates, and thus decreases the residence time estimate, of phosphorus in the ocean ([Tables 3 and 4](#)).

The source of phosphorus for incorporation into CFA in the early diagenetic regime is solid-phase phosphorus liberated either by microbial mineralization of organic matter, or by release of phosphorus associated with iron oxyhydroxides upon reduction of the iron oxyhydroxide substrate once it is transported into suboxic or anoxic zones within sediments. Examination of SEDEX-generated phosphorus profiles from a number of studies show roughly mirror-image profiles of the

reservoirs representing phosphorus source: organic matter (organic phosphorus) and/or iron oxyhydroxides (iron-bound phosphorus), and phosphorus sink (CFA). Examples of such co-varying profiles are shown in [Figure 9](#), in which authigenic CFA is forming at the expense of organic-P in Mississippi Delta sediments ([Figure 9\(a\)](#), after [Ruttenberg and Berner, 1993](#)), whereas CFA is forming at the expense of iron-bound P in sediments from the North Atlantic Platform ([Figure 9\(b\)](#), after [Slomp *et al.*, 1996a,b](#)). These mirror-image profiles illustrate the transfer of phosphorus from initially deposited P-reservoirs to CFA, the authigenic phase that is secondarily formed in the sediment. Note that iron oxyhydroxides may also be authigenic, forming *in situ* in surficial oxidized regions of the sediment and subsequently liberating associated phosphate to pore water upon reduction, once buried below the redox boundary ([Figure 6](#)). Thus, iron-bound

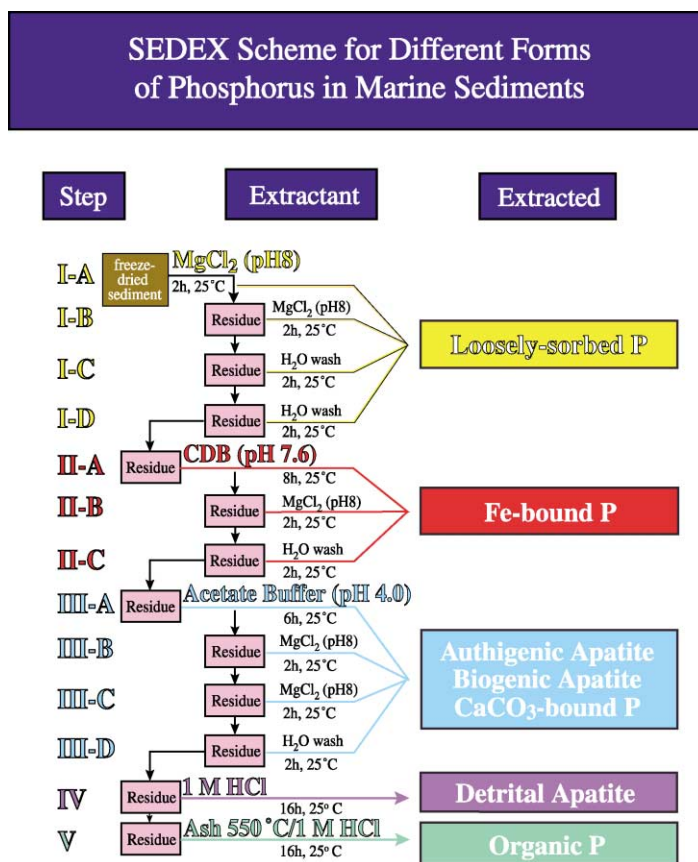


Figure 8 Sequence of extractants and extraction conditions that make up the SEDEX sequential extraction method for quantifying different forms of phosphorus in marine sediments (after Ruttenberg, 1992).

phosphorus may play an intermediate role in the transfer of phosphorus from organic matter to CFA in some depositional environments (see following discussion). The process of transfer from one phosphorus reservoir to another as a result of early diagenetic reactions has been termed “sink-switching” (Ruttenberg and Berner, 1993; Ruttenberg, 1993). This process can greatly enhance the retention of phosphorus by sediments (Ruttenberg and Berner, 1993; Slomp *et al.*, 1996a,b; Louchouart *et al.*, 1997; Filippelli, 2001), retaining phosphorus that would otherwise have been diffusively lost from sediments, and thus plays an important role in governing phosphorus burial rates and therefore residence time. Enhanced phosphorus retention in sediments by the mechanism of sink-switching of phosphorus from a phase that is unstable in the early diagenetic environment (labile organic phosphorus and ferric oxyhydroxides), to one that is stable (CFA), also impacts the global carbon cycle in that it permanently removes otherwise bioavailable phosphorus from the ocean.

An interesting variant to the sink-switching scheme is found in carbonate sediments hosting

seagrass beds, where pore-water fluoride and SEDEX analyses indicate CFA formation, but CFA does not accumulate because it is redissolved in the rhizosphere, where it provides an important source of phosphorus to otherwise P-limited seagrasses (Jensen *et al.*, 1998). Fluoride removal from pore water in carbonate sediments had been recognized in earlier studies and CFA was presumed to be the fluoride sink (Berner, 1974; Gaudette and Lyons, 1980). Rude and Aller (1991) cast some uncertainty on this conclusion, however, as they demonstrate that fluoride can be mobilized/immobilized by carbonate phases other than CFA.

Because the SEDEX scheme, like all sequential extraction schemes, is operationally defined, it is important to obtain corroborating evidence for the identity of the separately quantified sedimentary phosphorus reservoirs whenever possible. This can be accomplished by analyzing pore-water chemistry and other solid-phase components of the host sediments, and by linking depth profiles of various solutes and components to SEDEX phosphorus profiles. Some of the most elegant and comprehensive work of this type has been done by

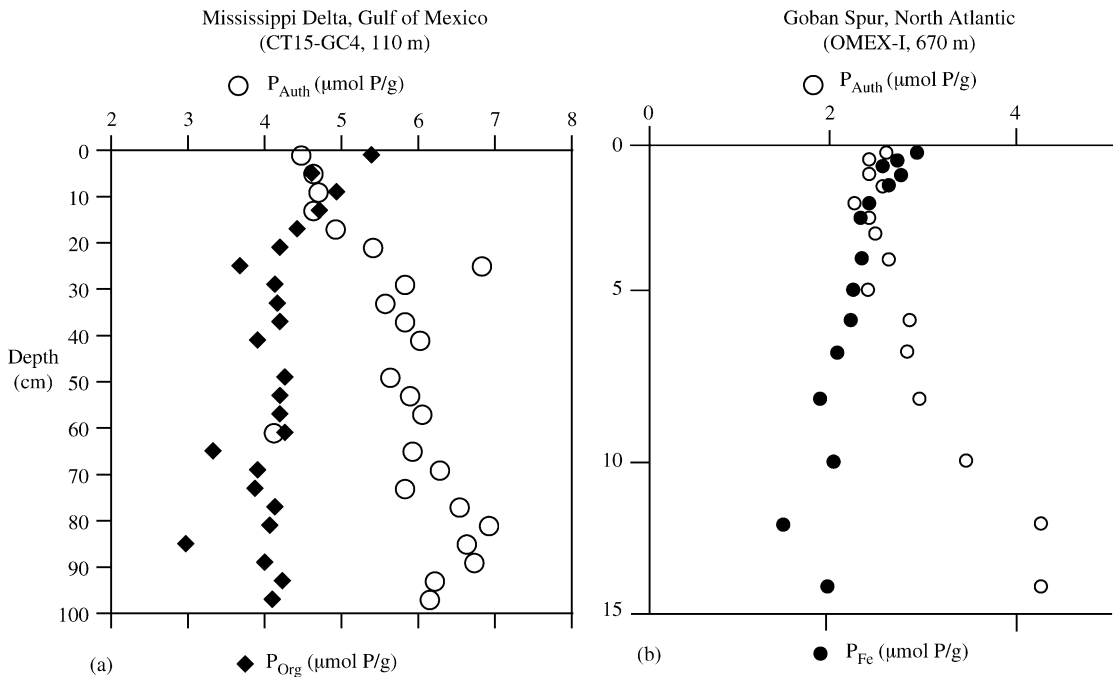


Figure 9 Sink-switching: Mirror-image SEDEX-generated phosphorus profiles from (a) the Mississippi Delta, showing formation of authigenic CFA at the expense of organic-P (after [Ruttenberg and Berner, 1993](#)), and (b) the Goban Spur on the North Atlantic Platform, showing CFA is forming at the expense of iron bound-P (after [Slomp *et al.*, 1996a,b](#)). These mirror-image profiles illustrate the transfer of phosphorus from initially deposited P-reservoirs to CFA, the authigenic phase that is secondarily formed in the sediment. Sink-switching is an important mechanism by which reactive phosphorus is retained in marine sediments.

[Slomp *et al.* \(1996a,b\)](#) in a study targeting early phosphorus diagenesis in North Atlantic continental platform sediments. In this study, application of a diagenetic model to pore-water and SEDEX-derived solid-phase phosphorus profiles indicates that CFA is forming at the expense of phosphorus bound to iron oxyhydroxides (Figure 9(b)). The model indicates that the iron-bound phosphorus forms *in situ* as phosphate released from decomposing organic matter is sorbed onto authigenic iron oxyhydroxides precipitating in the surficial oxidized layer of sediment. Once transported below the redox boundary by bioturbation, reduction of the host iron oxyhydroxides releases the iron-bound phosphorus, which is then incorporated into precipitating CFA. [Slomp *et al.* \(1996a,b\)](#) hypothesize that this mechanism, in which iron-bound phosphorus plays a key role in early diagenetic CFA formation, may be particularly important in sediments with low sedimentation rates where the most rapid organic matter mineralization takes place near the sediment–water interface. In such environments, sorption onto authigenic iron oxyhydroxides traps organic-matter-derived phosphate that would otherwise be diffusively lost from the sediments. [Slomp *et al.* \(1996a,b\)](#) propose that such a mechanism could also be at work in another

low-sedimentation environment, the Labrador Sea, where SEDEX phosphorus data indicate formation of CFA at the expense of iron-bound phosphorus ([Lucotte *et al.*, 1994](#)). In more rapidly accumulating sediments, organic phosphorus may be a more important direct source of phosphorus for CFA formation (e.g., Long Island Sound: [Ruttenberg and Berner, 1993](#); see Figure 9(a), the Oman Margin: [Shenau *et al.*, 2000](#)), while in still other sediments organic phosphorus and iron-bound phosphorus may both act as sources of phosphorus for CFA formation (the Mississippi Delta: [Ruttenberg and Berner, 1993](#); the Gulf of St. Lawrence: [Louchouart *et al.*, 1997](#)).

Experimental studies of authigenic apatite precipitation. Mechanisms and rates of authigenic apatite formation in the early diagenetic environment are difficult to resolve, because of the wide variety of biological, chemical, and physical factors that can affect its formation. Experimental studies of apatite formation under controlled conditions have provided important information for placing constraints on modes and rates of CFA authigenesis. Examples of such studies include those of [Ames \(1959\)](#), who documented nucleation of CFA on calcium carbonate; [Gulbrandsen *et al.* \(1984\)](#), who documented rates of CFA formation in seawater; [Jahnke \(1984\)](#), who evaluated the

effect of carbonate substitution on CFA solubility; Van Cappellen and Berner (1989, 1991), who focused on the idealized, noncarbonate-containing fluorapatite, to resolve dependence of growth rate on solution supersaturation, pH, temperature, and dissolved magnesium (believed to inhibit CFA formation: Martens and Harriss, 1970), and nucleation processes.

One process that has been explored experimentally, and invoked using field evidence, is the role of microbes in phosphogenesis. An unresolved question is whether this role is direct or indirect (see Krajewski *et al.*, 1994, for a review). The indirect role of microbial activity, that is microbial breakdown of organic matter and reduction of Fe-oxyhydroxides with subsequent pore-water phosphate buildup, is well documented and well accepted. Whether microbes play a direct role in CFA formation remains controversial. Petrographic and SEM evidence, showing phosphatized microbial remains in rocks and sediments, has been used to argue for microbes as both active and passive players in CFA formation (e.g., O'Brien *et al.*, 1981; Soudry and Champetier, 1983; Abed and Fakhouri, 1990; Lamboy, 1990). Experimental studies have also been devised to argue for a direct microbial role in apatite precipitation (e.g., Lucas and Prévôt, 1985).

Other Authigenic Phosphate Minerals. Although CFA has received the lion's share of attention in studies of authigenic phosphate minerals in marine sediments, there are other authigenic phosphate mineral phases that have intriguing diagenetic pathways, and may be important sinks for reactive phosphate from the oceans. Once such phase is authigenic vivianite, a hydrous ferrous phosphate with the chemical formula $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. The presence of this phase in marine sediments was first suspected as the result of pore-water studies of early diagenesis in a particularly organic-matter-rich, anoxic site in Long Island Sound, CT, USA: Sachem's Head (Martens *et al.*, 1978; Ruttenberg, 1991), and has also been observed in Amazon Fan sediments (Ruttenberg and Goñi 1997a,b). Sediments at both these sites display the classic phosphate profile observed in situations of authigenic phosphate mineral (Figure 3): an initial buildup in pore-water phosphate due largely to organic matter remineralization, and the reversal to a negative gradient at depth, reflecting removal of phosphate to the solid phase (Figure 10). The Sachem site is extremely anoxic, as evidenced by a rapid decline of sulfate to complete disappearance of sulfate by ~45 cm depth (Martens *et al.*, 1978). Pore-water-dissolved ferrous iron is undetectable until all of the sulfate has been converted into sulfide and precipitated out as ferrous sulfide, at which point ferrous iron is allowed to buildup in

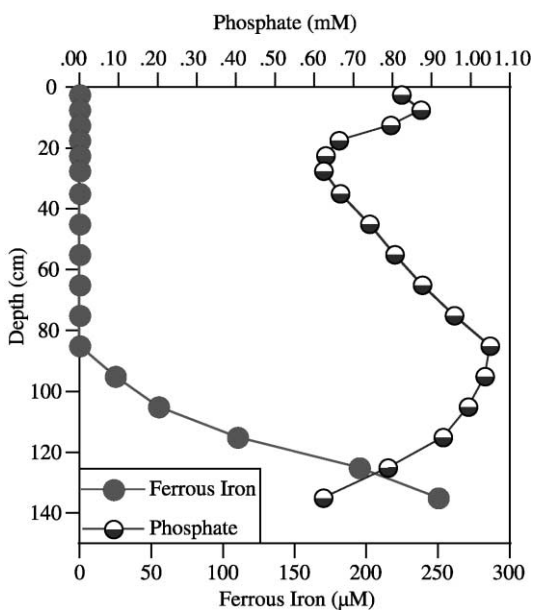


Figure 10 Authigenic vivianite formation: Pore-water-dissolved phosphate and ferrous iron profiles from Sachem's Head, Long Island Sound (phosphate data from Ruttenberg, unpubl., iron data from Canfield, unpubl.). Similar profiles were observed by Martens *et al.* (1978). Removal of phosphate coincident with buildup of ferrous iron in pore waters, as well as saturation state calculations, are suggestive of authigenic vivianite formation. Shallow subsurface phosphate maximum is likely due to non-steady-state deposition of organic matter, possibly after a phytoplankton bloom.

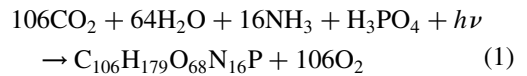
pore waters. Coincident with the appearance of ferrous iron in pore waters, pore-water phosphate concentrations begin to drop, indicating probable removal into vivianite (Figure 10). In Sachem's Head and Amazon Fan sediments, sulfide is depleted above the zone of iron and phosphate uptake, due to a high burden of solid-phase iron in these sediments. After the point of sulfide depletion, some of the ferrous iron that builds up in pore water is taken out of solution by formation of authigenic vivianite. This is supported by saturation state arguments (Martens *et al.*, 1978; Berner, 1990; Ruttenberg, 1991), and in the case of Amazon Fan Sediments, nodules of vivianite were recovered providing visible confirmation of processes deduced from indirect pore-water evidence (Ruttenberg and Goñi, 1997a,b). The prevalence of vivianite as an early diagenetic authigenic phosphate phase in the oceans has not been estimated, but it should be restricted to environments with a heavy burden of reactive iron oxyhydroxides, such that they are not completely consumed by iron sulfide formation and may supply ferrous iron for vivianite formation after sulfide has been completely consumed. Deltaic marine environments are prime candidates for

such a regime, and if vivianite is an important mechanism for phosphate removal in such environments, it is possible that it could contribute significantly to phosphate removal from the oceans.

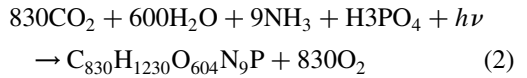
Both vivianite and CFA are authigenic minerals that have been detected in muddy sediments of the ocean's margins, and the type of processes involved in their formation, e.g., organic matter diagenesis and redox cycling causing a buildup of pore-water phosphate to the extent that supersaturation with respect to authigenic phosphate minerals form, have been envisaged as most important, if not exclusively important, in muddy sediments with high organic matter content. However, in a very different kind of environment, a different set of authigenic phosphate minerals have been detected and quantified, which may form an important and until recently unrecognized sink for reactive marine phosphorus. These are the authigenic aluminophosphates, often rare earth element (REE)-enriched, that have been found in marine sandstones through exacting scanning electron microscope analyses (Rasmussen, 1996, 2000; see Table 4). The dominant mineral in this assemblage is florencite ((REE)Al₃(PO₄)₂(OH)₆), with minor amounts of crandallite (CaAl₃(PO₄)₂(OH)5H₂O), gorceixite (BaAl₃(PO₄)₂(OH)5H₂O), and xenotime (YPO₄). These minerals appear to be ubiquitous, but volumetrically minor in the sandstones studied; diagenetic textures and the presence of structural sulfate have been cited as evidence of their authigenic early diagenetic nature (Rasmussen, 2000). They have escaped detection in earlier studies because of their small crystal size (<10 μm), and the fact that they are insoluble in the extractants commonly used to quantify marine authigenic phosphate minerals (Rasmussen, 2000). Studies conducted thus far have focused on sandstones of Early Cretaceous age or older (Rasmussen, 2000), so the formation of these phases in the modern ocean remains to be documented. However, based on the calculations of Rasmussen (2000), the phosphorus burial flux associated with these authigenic phases may exceed that of authigenic CFA, and thus impact estimates of residence time to an extent that would require a reassessment of the implications of an even shorter phosphorus residence time than has been proposed (Table 3).

Sedimentary organic carbon to organic phosphorus ((C:P)_{org}) ratios. Sediments are the repository of marine organic matter produced in overlying waters (autochthonous organic matter), as well as organic matter transported from the continents, dominantly through riverine transport, with minor atmospheric flux (allochthonous organic matter) (Figure 1, Table 2). The carbon and phosphorus cycles in both marine and terrestrial

systems are linked through their coupled uptake during photosynthesis, as illustrated by the following two equations, representative of photosynthetic fixation of carbon and nutrients at sea, by marine phytoplankton:



and on land, by terrestrial plants:



As a result of the coupled C- and P-uptake, the (C:P)_{org} ratio of organic matter preserved in marine sediments can, in theory, be used to make inferences about the coupled carbon and phosphorus cycles.

Since the early 1980s, there has been a focused effort to define and understand organic carbon to organic phosphorus ratios (hereafter (C:P)_{org}) in marine sediments. The motivation for this work stems from two research objectives. First, and foremost, by virtue of the coupled uptake of phosphorus and carbon during marine photosynthesis, and due to the fact that over long timescales it is likely that phosphorus is the limiting nutrient for oceanic biological productivity (Holland, 1978; Broecker and Peng, 1982; Codispoti, 1989; Smith, 1984; also see Section 8.13.3.3.4), various researchers have used the sedimentary (C:P)_{org} to hind-cast levels of marine biological productivity during different periods of Earth's history (Holland, 1984; Sarmiento and Toggweiler, 1984; Delaney and Boyle, 1988; Delaney and Filippelli, 1994; Van Cappellen and Ingall, 1994a,b; Delaney, 1998). Some of these research efforts are summarized in later sections of this chapter (see Section 8.13.3.4). A second objective has been to use the distinct (C:P)_{org} ratios of marine and terrestrial organic matter, in much the way that (C:N)_{org} ratios traditionally have been used (e.g., Ruttenberg and Goñi, 1997a,b), to determine sources of organic matter in marine sediments. In other words, these ratios can potentially be used to evaluate the relative partitioning of the sedimentary organic matter pool between marine and terrestrial organic matter sources.

In order to make sense of observed trends in sedimentary (C:P)_{org} ratios, and to evaluate the utility of this parameter in hind-casting past ocean productivity or in partitioning sedimentary organic matter as to source, it is important to understand the sources of organic matter to sediments, and the processes that modify the (C:P)_{org} ratio while organic matter is in transit to sediments, and then during its burial history. The (C:P)_{org} ratios of marine and terrestrial organic matter are distinct. This ratio in marine phytoplankton hovers closely around the classical

Redfield ratio of 106C : 1P, and whereas deviations from this ratio due to such things as phytoplankton nutritional status and environmental factors have been observed (e.g., Goldman *et al.*, 1979; Goldman, 1986), the adherence to the canonical 106 : 1 ratio by marine phytoplankton, first pointed out by Redfield (1958; see also Redfield *et al.*, 1963) is truly remarkable. In contrast, the (C : P)_{org} ratio observed in terrestrial plants can vary quite widely, but is always substantially enriched in carbon relative to phosphorus. This C-enrichment is illustrated by the 830C : 1P ratio given in Equation (2), which represents a reasonable average for terrestrial, vascular plants. The high (C : P)_{org} ratios of terrestrial vascular plant tissue are due to the dominance in these tissues of cellulose, a polymer of glucose, whereas phosphorus-containing biochemicals are a relatively minor component. Even considering the variability that has been observed for both phytoplankton and terrestrial plants, the distinction between the (C : P)_{org} ratios of marine versus terrestrial organic matter is robust.

An overview of previous studies on (C : P)_{org} ratios has been compiled recently (Anderson *et al.*, 2001), which nicely summarizes the various observations and interpretations of different workers in the field (Table 6). All of the studies summarized in Table 6 report observing (C : P)_{org} ratios greater than the Redfield ratio, particularly in organic-rich, continental margin sediments. Most of these studies interpret the higher ratios, which often increase with depth below the sediment–water interface, as a reflection of preferential regeneration of phosphorus relative to carbon during microbial mineralization of marine organic matter. This has been a well-accepted concept in the field of early diagenesis for some time (e.g., Berner, 1980; Ingall and Van Cappellen, 1990), and has been understood to reflect the more labile nature of P-biochemicals relative to most nonphosphorus containing organic carbon compounds. A second rationale for this observation has been that, because phosphorus is an essential and potentially limiting nutrient, it is preferentially targeted for remineralization to support subsequent biological productivity. The paradigm of preferential regeneration of phosphorus relative to carbon suggests that progressively more extensive mineralization should lead to ever higher (C : P)_{org} ratios. However, in contradiction to this paradigm, several studies have observed sedimentary (C : P)_{org} ratios close to the Redfield ratio in pelagic sediments (Froelich *et al.*, 1982; Ingall and Van Cappellen, 1990; Ruttenberg, 1990) and in iron-dominated Amazon Shelf sediments (Ruttenberg and Goñi, 1997a), both of which are sites of intensely remineralized organic matter. In the pelagic environment the high degree of organic matter

degradation is due to low sediment accumulation rates and long oxygen exposure times, whereas in Amazon Shelf sediments it is due to prolonged oxygen exposure due to repeated resuspension into the water column, under conditions that have been likened to a fluidized bed reactor (Aller, 1998). This observation does not fit into the paradigm of preferential regeneration of phosphorus relative to carbon with progressively more extensive mineralization. The explanations variously given for this unexpected observation are either that sedimentary organic matter at these sites is enriched in refractory organic phosphorus compounds, left behind after extensive remineralization of more labile organic carbon, or that these low ratios reflect living sedimentary bacterial communities or their residua (Froelich *et al.*, 1982; Ingall and Van Cappellen, 1990; Ruttenberg and Goñi, 1997a).

Ingall and Van Cappellen (1990) systematized the range of (C : P)_{org} ratios observed in different depositional environments by relating them to sediment accumulation rate (Figure 11). Sediment accumulation rate has been recognized as a robust proxy for extent of organic carbon degradation (e.g., Henrichs and Reeburgh, 1987; Berner, 1989; Canfield, 1989), and thus it is reasonable to expect that it may also be a proxy for extent of P_{org} degradation. The rationale given for the observed relationship between sedimentary (C : P)_{org} ratios and sediment accumulation rate (Figure 11) is as follows. In the highest sedimentation rate region, (C : P)_{org} ratios approximate the Redfield ratio because organic matter has very little time to decompose before it is buried into the zone of less efficient, anoxic diagenesis. Therefore, minimal P_{org} is regenerated preferentially to C_{org}, and the organic matter buried has a (C : P)_{org} ratio closely approximating the Redfield ratio for fresh phytoplankton. In the lowest sediment accumulation rate region, the near-Redfield (C : P)_{org} ratios are explained as either residual organic matter rich in refractory organic phosphorus compounds, bacterial biomass, or both. In the mid-range of sediment accumulation rates the high (C : P)_{org} ratios suggest preferential P_{org} regeneration relative to C_{org} during incomplete mineralization of organic matter. The sediment accumulation rate framework appears to work well for medium to high sedimentation rates. The explanation of low (C : P)_{org} ratios in low sediment accumulation regions is substantially weaker, however. Attempts to identify the nature of refractory organic phosphorus compounds that can withstand the most intense remineralization regimes have not been successful (e.g., Section 8.13.3.3.2 cites studies in which the two most promising candidates for refractory P_{org} are discounted: phosphonates—Laarkamp, 2000; Laarkamp and Ruttenberg, 2000; Ruttenberg and Laarkamp, 2000; and inositol phosphates—Suzumura and Kamatani, 1996).

Table 6 Overview of Previous Studies on (C:P)organic Ratios in Marine Sediments (after Anderson *et al.*, 2001).

| # | References | Geographic region | Water depth range (m) | Observations and interpretations |
|---|-------------------------------|---|---|--|
| 1 | Hartmann <i>et al.</i> (1973) | Northwest African continental slope | 2037–2066 | (C:P) _{org} increased with increasing sediment depth to a ratio of ~265 at depths >90 cm. |
| 2 | Hartmann <i>et al.</i> (1976) | Northwest African continental slope | ~600–3700 (also on shelf core) | Preferential decomposition of P _{org} compounds relative to C _{org} . (C:P) _{org} increased with increasing sediment depth; higher (C:P) _{org} in rapidly depositing sediments (>480 for >11 cm kyr ⁻¹) than in slowly depositing sediments (<240 for <6 cm kyr ⁻¹). |
| 3 | Filipek and Owen (1981) | Gulf of Mexico | 30 and 112 | Preferential decomposition of P _{org} compounds during early diagenesis; formation of authigenic P compounds. (C:P) _{org} increased with increasing sediment depth to a mean ratio of 207 in shallow and 259 in deep station. |
| 4 | Krom and Berner (1981) | Long Island Sound | 9 | Preferential decomposition of P _{org} compounds; formation of authigenic P compounds. (C:P) _{org} constant (320) with increasing sediment depth; mobilization of P via metal oxide dissolution within zone of bioturbation only. |
| 5 | Suess (1981) | Peru continental margin | 180–645 | C _{org} delivered to sediment depleted in P _{org} relative to Redfield Ratio for marine phytoplankton. (C:P) _{org} > Redfield Ratio at all sediment depths. Fish debris dissolution significant source of interstitial dissolved phosphate |
| 6 | Froelich <i>et al.</i> (1982) | Northwest African continental margin; west African continental margin, French equatorial Atlantic; eastern tropical Pacific (MANOP sites M and H); western subtropical Atlantic, east North American continental slope and rise; Gulf of Mexico; Santa Barbara Basin, Long Island Sound; Peru continental margin; central Pacific gyre (includes data sets from references 1–5) | Continental margin to open ocean water depths | P _{org} concentrations in marine sediments relatively constant; (C:P) _{org} > Redfield Ratio in organic rich sediments, <Redfield Ratio in organic carbon poor sediments (<1 wt% C _{org}). Preferential decomposition of P _{org} compounds; organic carbon poor sediments enriched in stable, P-rich moieties. |

| | | | | |
|----|---------------------------------|---|---|--|
| 7 | Mach <i>et al.</i> (1987) | Data set from Froelich <i>et al.</i> (1982) plus additional Peru sites | Continental margin to open ocean water depths | <p>P_{org} concentrations in marine sediments linearly related to C_{org}; $(C:P)_{org} > \text{Redfield Ratio}$.</p> <p>Earlier conclusions from same data set were incorrect because of problems with analytical detection limits and difference methods.</p> |
| 8 | Ingall and Van Cappellen (1990) | Amazon Delta, eastern equatorial Atlantic; eastern equatorial Pacific; Long Island Sound; Mississippi Delta; Northwest African continental margin; Pacific deep sea; Peru continental margin; Santa Barbara Basin; western Gulf of Mexico (includes data sets from references 2, 3, 5, and 6; from Sholkovitz, (1973), Froelich <i>et al.</i> , (1988), Ruttenberg, (1990), and their own data) | Continental margin to open ocean water depths | <p>$(C:P)_{org}$ varies with sedimentation rate: <200 at sedimentation rates <2 and $>1000 \text{ cm kyr}^{-1}$, and up to 600 at intermediate sedimentation rates.</p> <p>Preferential decomposition of C_{org} relative to P_{org} occurs during oxic respiration, leaving behind P_{org} enriched organic matter, whereas preferential decomposition of P_{org} during incomplete degradation of organic matter under anoxic conditions leaves organic matter depleted in P_{org} relative to C_{org}.</p> |
| 9 | Ruttenberg and Berner (1993) | Long Island Sound; Mississippi Delta | 9 and 110 | <p>$(C:P)_{org} > \text{Redfield Ratio}$, accompanied by transformation of P_{org} to carbonate fluorapatite. This “sink switching” results in enhanced P-retention by sediments.</p> |
| 10 | Ingall <i>et al.</i> (1993) | Various shale sequences, both bioturbated and laminated, especially from the Camp Run Member of the New Albany Shale (Late Devonian-Early Mississippian age) | | <p>$(C:P)_{org} \sim 150$ for bioturbated shales; ~ 3900 for laminated shales.</p> <p>High $(C:P)_{org}$ in anoxic sediments results from limited bacterial storage of P; extensive P-regeneration, and enhanced C_{org} preservation.</p> |
| 11 | Calvert <i>et al.</i> (1996) | Reexamination of Camp Run Member of the New Albany Shale | | <p>Sediment sources and water depths were different during deposition of bioturbated and laminated shale sequences, making comparison of the two difficult.</p> |

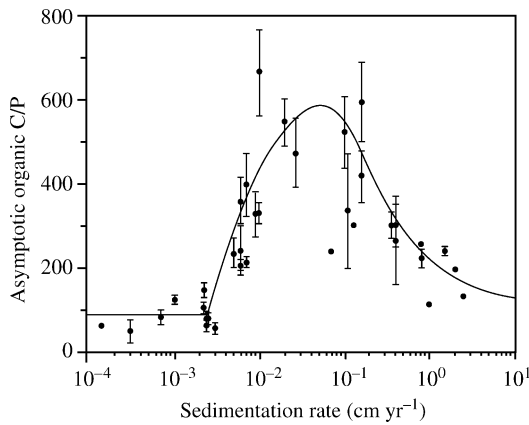


Figure 11 Calculated asymptotic organic C : P ratios plotted as a function of sedimentation rate. Designation of these (C : P)_{org} ratios as “asymptotic” derives from the fact that they represent the composition of organic matter buried below the depth at which the (C : P)_{org} increases, and so reflect the composition of buried (preserved) organic matter. Error bars represent the standard deviation of the average asymptotic (C : P)_{org} values, or the absolute range of values where their number was less than or equal to 3. Solid curve is the model-predicted asymptotic (C : P)_{org} ratio versus sedimentation rate. See text for discussion (after Ingall and Van Cappellen, 1990).

The possibility of sediment enriched in bacteria or their remains is a viable explanation, but such an enrichment in bacteria has not been conclusively demonstrated. Another weak point in the Ingall and Van Cappellen study, and in most other studies of (C : P)_{org} in marine sediments, is the failure to recognize explicitly that, particularly in continental margin settings, terrestrial organic matter may significantly affect the observed (C : P)_{org} ratios in marine sediments. In these environments, one should expect the sedimentary (C : P)_{org} ratios to reflect a mixture of marine and terrestrial organic matter (e.g., Ruttenberg and Goñi, 1997a, Ruttenberg and Goñi, 1997b). In sites where the observed sedimentary (C : P)_{org} ratios exceed the Redfield ratio, for example, it is difficult to evaluate whether these high ratios reflect preferential phosphorus regeneration from autochthonous marine phytodetritus, the presence of allochthonous, high-(C : P)_{org} ratio terrestrial organic matter, or both. Thus, there remain many open questions about what, in fact, sedimentary (C : P)_{org} ratios represent. As a result, it remains unclear how best to interpret marine sedimentary (C : P)_{org} ratios, which are a complex reflection of source material, depositional environment, extent of degradation, and degradation pathway.

In a departure from the work summarized in the foregoing paragraphs, Anderson *et al.* (2001) argue that the parameter of interest for reconstructing marine paleoproductivity is not the sedimentary

(C : P)_{org} ratio, but the ratio of organic carbon to reactive phosphorus (hereafter, C_{organic} : P_{reactive}), where P_{reactive} is defined (as it is in Table 2, note (f)), as the sum of SEDEX-quantified organic-, authigenic-, loosely sorbed-, and iron-bound phosphorus. The rationale for preferred use of the C_{organic} : P_{reactive} ratio is that, because of diagenetic sink-switching (see Section 8.13.3.3.2), the phosphorus contained in the SEDEX-quantified authigenic-, loosely sorbed-, and iron-bound phosphorus pools derived originally from P_{org}. Thus, the quantity P_{reactive} is a reflection of the P_{org} originally deposited with sediments. Two potential weaknesses of this model are that (i) it implies 100% P-retention by sediments, which is likely not a good assumption as, except in the most rapidly accumulating sediments, it is expected that some remineralized P_{org} will diffuse out of sediments; and (ii) it does not take into account the sizeable authigenic-P “background” that has been found in most SEDEX studies (e.g., Ruttenberg and Berner, 1993; Slomp *et al.*, 1996a,b; Louchouart *et al.*, 1997). If this background pool is not truly authigenic phosphorus, i.e., if it is a detrital phase that was passively deposited and did not derive its phosphorus from organic matter (e.g., see discussion in Ruttenberg and Berner (1993)), then the C_{organic} : P_{reactive} ratio will be systematically offset. Despite these potential weaknesses, Anderson *et al.* (2001) make an interesting and compelling case for use of the C_{organic} : P_{reactive} ratio in lieu of the traditional (C : P)_{org} ratio. Further, their results lead them to question whether sediment accumulation rate and state of anoxia exert strong control on sedimentary (C : P)_{org} ratios, as has been argued in earlier studies (e.g., Ingall and Van Cappellen, 1990; Ingall *et al.*, 1993). There remain substantial questions about what, precisely, the sedimentary (C : P)_{org} ratios, or C_{organic} : P_{reactive} ratios represent. The degree of uncertainty in results of models employing these ratios to infer past variations in coupled carbon and phosphorus cycling will continue to challenge scientists, until these questions can be further resolved.

Coupled Iron-phosphorus Cycling. The affinity of phosphate for sorptive association with ferric oxide and oxyhydroxide phases, well documented in soil and freshwater systems (see Sections 8.13.3.1 and 8.13.3.2), is also a well-studied process in marine systems. Three distinct marine environments where coupled iron–phosphorus cycling has been identified as an important process are MOR systems, estuaries, and continental margin sediments. The purely physico-chemical process of sorption is essentially the same in these three distinct environments, where an initial, rapid surface sorption phase is followed, given enough time, by a redistribution of adsorbed phosphate into the interior of iron oxyhydroxides by solid-state diffusion (Bolan *et al.*, 1985;

Froelich, 1988). The quantity of phosphate sorbed depends upon the nature of the ferric iron phase, with less crystalline phases having higher surface area and therefore more sorption capacity (Bolan *et al.*, 1985; Ruttenger, 1992). The specific characteristics of the different environments, however, impact the timescale and the pattern of this coupled cycling, and the ultimate fate of the iron and phosphorus that are entrained in the coupled cycling process. Each of these environments will be discussed in turn.

Sorptive removal of phosphate by iron oxyhydroxides in hydrothermal MOR environments was first documented in a study of the East Pacific Rise MOR system by Berner (1973), who recognized that these environments could constitute a significant sink for phosphate from the ocean. Subsequent work has expanded on this initial study, focusing on phosphate scavenging onto volcanogenic ferric oxyhydroxides in water column hydrothermal plumes above MORs (Feely *et al.*, 1990; Rudnicki and Elderfield, 1993), and removal in ridge-axis and ridge-flank hydrothermal systems at different MOR systems throughout the world's oceans (Froelich *et al.*, 1977; Wheat *et al.*, 1996). The more recent studies confirmed earlier suggestions of phosphate uptake by ridge-flank basalts, which had been inferred from highly correlated phosphate and ferric iron concentrations in progressively altered seafloor basalts (Hart, 1970; Thompson, 1983). By the latest estimates (Wheat *et al.*, 1996), MOR ridge-flank systems and water column hydrothermal plume particles dominate phosphorus removal at MOR systems, removing approximately 22% and 27%, respectively, of the preindustrial dissolved riverine phosphorus flux into the oceans. Plume particles form when ferrous

iron exhaled from MOR vents encounters the cold, oxidized oceanic waters above the vents, and precipitates out as amorphous ferric oxyhydroxide particles (Figure 12). Phosphate is scavenged onto these volcanogenic ferric oxyhydroxides by co-precipitation and surface sorption. As hydrothermal plumes reach a state of neutral buoyancy and are advected away from the ridge axis, fallout from these plumes drapes the seafloor beneath with reactive ferric oxyhydroxides and their associated phosphorus. Scavenging of phosphorus in ridge-flanks occurs via basalt–seawater reactions promoted by hydrothermally driven seawater circulation through oceanic crust (Figure 12). Whereas phosphate removal with hydrothermal plume particles and in un-sedimented segments of MOR systems clearly occurs by sorption onto volcanogenic ferric oxyhydroxides, some component of phosphate removal in ridge-flank sediments may be due to authigenic apatite formation. Pore-water phosphate and fluoride gradients in sediments deposited on ridge flanks at some sites are consistent with authigenic apatite (CFA) formation (Wheat *et al.*, 1996), but the relative importance of CFA versus sorption onto Fe-oxyhydroxides as removal mechanisms for phosphate in MOR systems has not been determined. The magnitude of phosphorus removal at MOR systems suggests that any changes in hydrothermal activity at MOR in the past or in the future could perturb the magnitude of this sink, and thus have significant impact on the global phosphorus cycle (Wheat *et al.*, 1996).

The mixing of seawater and freshwater in estuaries causes coagulation and flocculation of metal-organic rich colloidal material (Sholkovitz *et al.*, 1978; Fox, 1990), and estuarine water

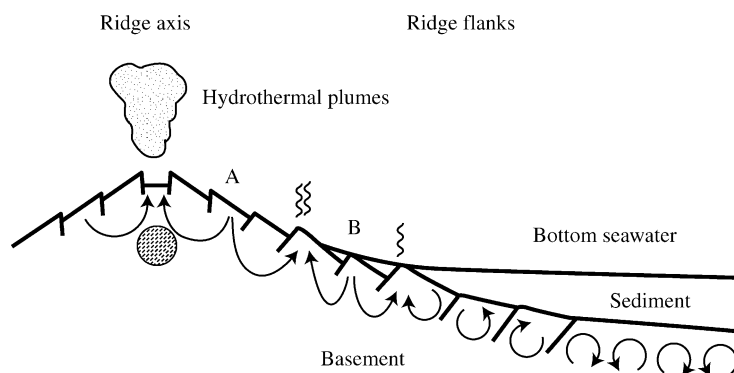


Figure 12 Conceptual model of seawater circulation through oceanic crust on the flanks of MOR systems (after Wheat *et al.*, 1996). Circulation cell A illustrates the case where bottom seawater enters basement directly through faults and basaltic outcrops, and there is no direct contact with sediment, while circulation cell B illustrates the case where seawater downwells through the sediment into basement and interacts with sediment along its flow trajectory. Phosphate is removed in both instances via sorption onto ferric oxyhydroxides. At sediment covered ridge-flank segments, additional P-removal as authigenic CFA may occur as a result of diagenesis and sink-switching within the sediments. In addition, ferric oxyhydroxides precipitating out of hydrothermal plumes, formed as hot hydrothermal water is vented from the ridge axis, scavenge phosphate from seawater (see text for discussion).

columns often have a high concentration of suspended sediments due to riverine input of particulates, and due to resuspension of bottom sediments. It has been shown both in laboratory and field studies that suspended sediments influence the concentration of dissolved phosphorus in a process that has been termed “phosphate buffering” (e.g., Carritt and Goodgal, 1954; Pomeroy *et al.*, 1965; Chase and Sayles, 1980; Lucotte and d’Anglejan, 1983; Fox *et al.*, 1985, 1986; Fox, 1989; Lebo, 1991; see Section 8.13.3.2.2). This buffering mechanism causes dissolved phosphate levels to remain relatively constant, and has been attributed to solid-phase sorption. It is widely believed that ferric oxyhydroxides are the prime substrates for phosphate sorption in estuaries (e.g., Fox, 1989). The overall effect on phosphorus in estuaries, however, is complicated by other process such as biological uptake, and periodic seabed storage and diagenesis followed by resuspension, such that the role of estuaries as sources or sinks of phosphorus to the oceans is variable, and cannot be generalized (Froelich *et al.*, 1982; Kaul and Froelich, 1996; Vink *et al.*, 1997).

In marine continental margin sediments, coupled cycling of iron and phosphorus is a dynamic phenomenon. In river-dominated margins, detrital iron-bound phosphorus of variable reactivity is delivered to marine sediments (Berner and Rao, 1994; Ruttenberg and Canfield, 1994). Whether these phases participate in redox cycling during subsequent diagenesis depends upon the lability of the iron mineral substrate. Within sediments (as shown schematically in Figure 6), a portion of the pore-water phosphate derived from organic matter mineralization that does not escape to overlying waters via diffusion may be sorbed to detrital or authigenic iron oxyhydroxides within the oxidized zone of the sediment (e.g., Krom and Berner, 1980; Sundby *et al.*, 1992; Slomp and Van Raaphorst, 1993; Jensen *et al.*, 1995; Slomp *et al.*, 1996a,b). Once buried into the reduced zone of sediments, the ferric oxyhydroxide substrate is subject to reductive solubilization, and concomitant phosphate release to pore waters. Both the dissolved ferrous iron and phosphate can then diffuse upward into the oxidized zone, where the iron is subject to reoxidation, and the phosphate to renewed scavenging by the freshly precipitated ferric oxyhydroxide (Heggie *et al.*, 1990; Sundby *et al.*, 1992; Jensen *et al.*, 1995; Slomp *et al.*, 1996a,b). Alternatively, the phosphate released within the reduced zone of sediments may be taken up by authigenic minerals (Van Cappellen and Berner, 1988; Heggie *et al.*, 1990; O’Brien *et al.*, 1990; Slomp *et al.*, 1996a,b; Reimers *et al.*, 1996).

The oxidized zone can be of variable thickness, depending on a host of environmental parameters,

including sediment accumulation rate, organic matter concentration and reactivity, bottom-water oxygen, infaunal activity, and physical resuspension processes. Many of these parameters vary seasonally, and as such, the coupled cycling of iron and phosphorus can have a distinct seasonality (Lijklema, 1980; Aller, 1980; Jensen *et al.*, 1995; Colman and Holland, 2000). In summer the oxidized zone will decrease due to increased organic matter loading and enhanced microbial activity at warmer summer temperatures. In winter, the oxidized zone will expand due to a reversal of these conditions. These parameters can also vary spatially due, for example, to variability in bottom-water topography or in overlying water conditions that can affect organic matter productivity and subsequent organic loading of underlying sediments. This spatial and temporal variability affects another important phenomenon in the marine phosphorus cycle, that of the return phosphate flux out of marine sediments into overlying waters, or the benthic phosphate flux.

Benthic Return Flux of Phosphorus From the Seabed. A number of diagenetic processes act to enrich pore-water phosphate concentrations above bottom water levels and, as a result, can lead to an appreciable benthic return flux of phosphate from the seabed to overlying bottom waters. These processes, discussed in earlier sections of this chapter (see Figures 1, 3, and 6) include (i) microbial respiration of organic matter in sediments; (ii) microbial reduction and solubilization of ferric oxyhydroxides with subsequent release of associated phosphate (iron-bound phosphorus (P_{Fe})); and (iii) abiotic reduction of ferric oxyhydroxides by H_2S and liberation of P_{Fe} (Krom and Berner, 1981). Although not explicitly demonstrated in marine sediments, several studies in freshwater systems also suggest that bacteria can liberate phosphate directly to pore waters in response to physiological cues tied to redox changes in the sedimentary environment (Shapiro, 1967; Gächter *et al.*, 1988; Gächter and Meyers, 1993; Carlton and Wetzel, 1988; however, see Gunnars and Blomqvist (1997)). The most extreme contrasts between pore-water and bottom-water phosphate concentrations occur in organic-rich, anoxic marine sediments, typically in continental margin environments, where phosphate concentrations can reach levels of 100–500 μM phosphate in the upper 10 cm below the sediment–water interface, in contrast to bottom water phosphate concentrations of 2–3 μM (e.g., Krom and Berner, 1981; Klump and Martens, 1987; Ruttenberg and Berner, 1993; McManus *et al.*, 1997; Reimers *et al.*, 1996).

The magnitude of phosphate benthic flux can be estimated from the pore-water gradient, using Fick’s first law of diffusion (e.g., Krom and

Berner, 1981; Klump and Martens, 1981; Sundby *et al.*, 1992) corrected for bioturbation, bioirrigation, and abiotic mixing/irrigation where necessary (e.g., Berner, 1980; Aller, 1980, 1982; Klump and Martens, 1981), or by mass balance calculations (e.g., Krom and Berner, 1981; Klump and Martens, 1987). Alternatively, the benthic flux out of sediments can be measured directly during incubations of retrieved cores, or by deploying flux chambers to make *in situ* benthic flux measurements (e.g., Aller, 1980; Ingall and Jahnke, 1994, 1997; Jensen *et al.*, 1995; Klump and Martens, 1987; McManus *et al.*, 1997). Studies in which directly measured phosphate benthic fluxes are compared to the flux calculated from pore-water profiles often find that benthic fluxes obtained by these two approaches disagree (e.g., Krom and Berner, 1981; Klump and Martens, 1981, 1987; McManus *et al.*, 1997). Cases in which the pore-water gradient-derived flux is high relative to the directly measured benthic flux are typically explained by removal processes that occur at or near the sediment–water interface. These processes thus impede escape of pore-water phosphate from the seabed, but do not perturb the pore-water profile. Likely processes include phosphate sorption onto iron oxyhydroxides in the surficial oxidized layer of sediments, and biological uptake by interfacial microbial mats (Klump and Martens, 1981, 1987; Jensen *et al.*, 1995; Colman and Holland, 2000). Instances in which the pore-water gradient-derived flux is low relative to the directly measured benthic flux have been explained by rapid decomposition of highly labile organic matter right at the sediment–water interface, such that phosphate is liberated directly to bottom water and does not contribute to the pore-water buildup (e.g., Krom and Berner, 1981). While the *in situ* measurement approach may provide more accurate flux estimates, this approach is much less commonly taken because it requires specialized equipment, and is more time consuming (benthic chambers must be deployed for time periods of one to several days; e.g., McManus *et al.*, 1997; Berelson *et al.*, 1996) than core retrieval.

A number of studies have highlighted the role of bottom water and sediment redox state on the benthic return flux of phosphate (Klump and Martens, 1981, 1987; Sundby *et al.*, 1992; Ingall and Jahnke, 1994, 1997; Jensen *et al.*, 1995; McManus *et al.*, 1997; Colman and Holland, 2000). When there is sufficient oxygen in bottom waters to support formation of iron oxyhydroxides in surficial sediments, these can act as a trap for pore-water phosphate, diminishing or eliminating the benthic phosphate return flux (see previous discussion). Phosphate released from decomposing organic matter below the redox boundary is transported down the concentration gradient into

the oxic surficial zone of sediments, where it can be sorptively scavenged onto authigenic ferric oxyhydroxides (e.g., Figure 6). This may happen multiple times prior to ultimate burial (e.g., Jensen *et al.*, 1995). The development of an oxic surface layer in sediments can be a seasonal phenomenon, and the depth of the redox boundary below the sediment–water interface can likewise vary seasonally, in response to seasonal changes in temperature, temperature-sensitive metabolic processes, and organic matter flux to sediments (Aller, 1980; Klump and Martens, 1981, 1987; Sundby *et al.*, 1992; Jensen *et al.*, 1995; Colman and Holland, 2000).

Sorptive removal of phosphate from pore waters decouples phosphate from carbon during organic matter remineralization. Ingall and Jahnke (1994, 1997) have made a strong case for elemental fractionation of phosphorus from carbon during sediment diagenesis, and argue that phosphorus burial efficiency (relative to carbon) is reduced in low-oxygen continental margin environments, relative to environments with higher bottom-water oxygen. Drawing on a significantly larger data set, McManus *et al.* (1997) find that the picture is not necessarily as simple as that painted by Ingall and Jahnke (1994, 1997), and that some environments with low bottom-water oxygen do not show reduced phosphorus burial efficiency. Both of these studies utilized *in situ* benthic phosphate flux chamber data. In a synthesis of almost 200 pore-water phosphate profiles from the literature, Colman and Holland (2000) argue convincingly that the variability observed in the Ingall and Jahnke (1994, 1997) and McManus *et al.* (1997) studies could well be explained by seasonal variability. This argument is consistent with studies that have focused on measuring *in situ* benthic phosphorus flux on a seasonal basis (e.g., Aller, 1980; Klump and Martens, 1981, 1987), and have documented substantial differences in magnitude and direction of benthic flux as a function of season.

Mechanisms proposed to explain the relationship between bottom-water anoxia and phosphate benthic flux are (i) coupled iron–phosphorus cycling (Aller, 1980; Klump and Martens, 1981, 1987), and/or (ii) bacterial release of phosphate under anoxic conditions (Ingall and Jahnke, 1994, 1997, citing the work of Gächter *et al.*, 1988; Gächter and Meyers, 1993, in freshwater systems). It is likely that both mechanisms are operant, and both contribute to variability in benthic phosphate return flux and fractionation of phosphorus from carbon during organic matter mineralization (Colman and Holland, 2000). Drawing on their large and geographically diverse data set, Colman and Holland (2000) argue convincingly that the benthic phosphate return

flux is a quantitatively important term in the marine phosphorus budget. The link between the benthic phosphate return flux and oxidation state of bottom water/sediments, and the coupled cycling of phosphorus, iron, and carbon that results, has been proposed as a negative feedback that has stabilized atmospheric oxygen throughout the Phanerozoic (Betts and Holland, 1991; Colman and Holland, 1994, 2000; Holland, 1994; Colman *et al.*, 1997; see Section 8.13.3.4.2 for further discussion).

8.13.3.3 Phosphorus in the oceanic water column: composition and cycling

Dissolved inorganic phosphorus (DIP). Uncombined dissolved inorganic phosphorus exists as three ionic species in natural waters, corresponding to the conjugate bases of weak, triprotic phosphoric acid (H_3PO_4). In seawater of pH 8, the dominant species is HPO_4^{2-} (87%), over PO_4^{3-} (12%), and H_2PO_4^- (1%), (Kester and Pytkowicz, 1967). Since PO_4^{3-} is the ionic species taken up into authigenic minerals, it is necessary to have the apparent dissociation constants to evaluate the activity of this species for use in solubility calculations. In a series of experiments designed to evaluate the apparent dissociation constants of phosphoric acid in natural waters, Kester and Pytkowicz (1967) compared the distribution of phosphate species in freshwater, artificial seawater, and a sodium chloride solution of ionic strength identical to the

artificial seawater (Figure 13). This approach permitted distinction between nonspecific effects (e.g., those due to ionic strength only) and specific interactions (e.g., those resulting from interactions such as ion pair and complex formation). The shift in phosphate species distribution from freshwater (Figure 13(a)) to the 0.68 M NaCl solution (Figure 13(b)) is attributable to ionic strength effects, whereas the shift observed from NaCl to the artificial seawater solution (Figure 13(c)) is brought about by specific interactions between phosphate species and seawater dissolved cations. Kester and Pytkowicz (1967) estimated that 99.6% of the PO_4^{3-} and 44% of the HPO_4^{2-} species are complexed by cations other than Na^+ , dominantly by Mg^{2+} and Ca^{2+} . For the that portion of the DIP pool present as cation-complexes, Atlas *et al.* (1976) estimate that various Mg-phosphate complexes dominate (43%), followed by Na- (15%) and Ca-phosphate (12%) complexes (Figure 14).

Polyphosphate, another form of DIP, is a polymer of phosphate that accumulates intercellularly in phosphate-replete phytoplankton and bacteria (e.g., Solórzano and Strickland, 1968, and citations therein). Attempts to measure polyphosphate in seawater have been limited. Solórzano and Strickland (1968) found barely detectable levels in two coastal studies, and speculate that any polyphosphate formed by marine organisms that is liberated to seawater is likely rapidly reused

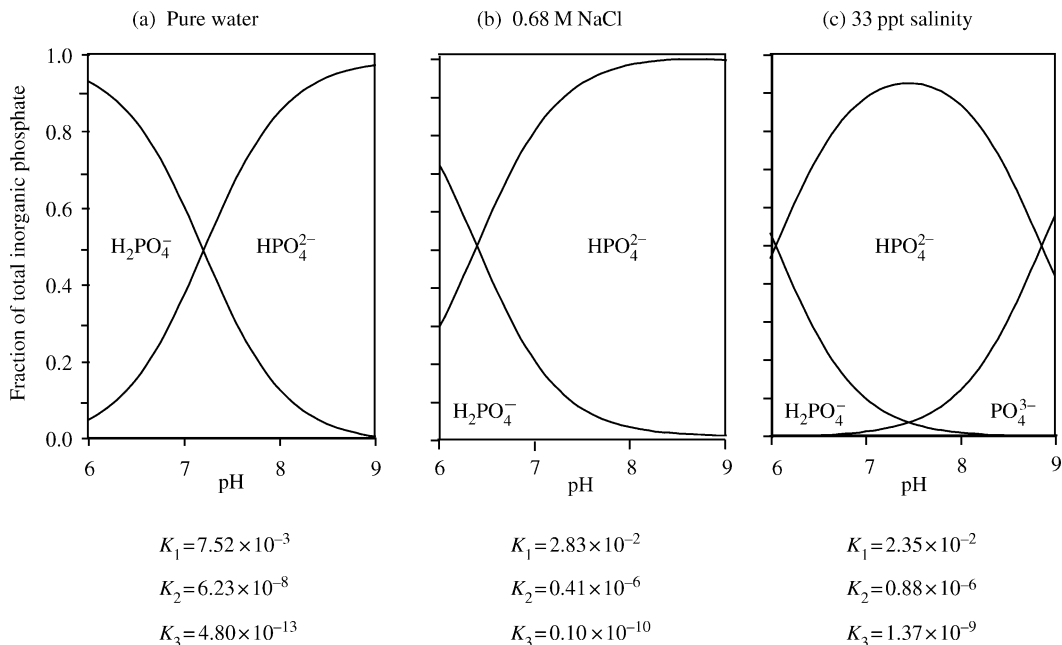


Figure 13 Distribution of phosphoric acid species as a function of pH, and dissociation constants, in (a) pure water; (b) 0.68 M NaCl; and (c) artificial seawater of salinity 33 ppt (after Kester and Pytkowicz, 1967).

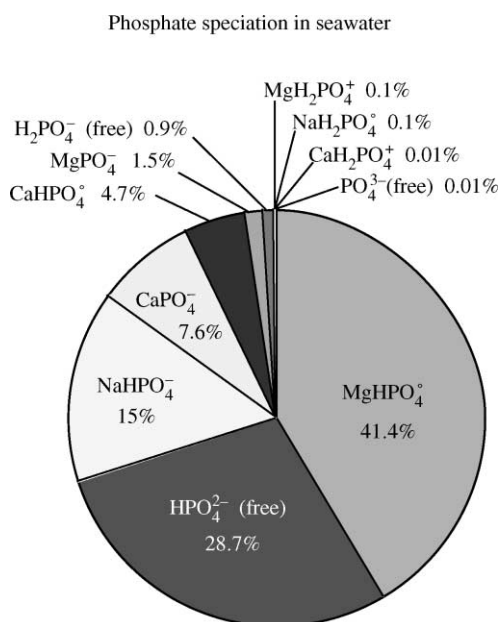


Figure 14 Calculated speciation of inorganic phosphate in seawater at 20 °C, 34.8 ppt salinity, and pH 8 (after Atlas *et al.*, 1976).

by phytoplankton and bacteria, owing to its high degree of bioavailability, and therefore its accumulation in seawater is highly unlikely.

The fundamental characteristics of the oceanic distribution of phosphate were summarized earlier (Section 8.13.2.3, and Figure 1). Levitus *et al.* (1993) present average nutrient distributions in the global ocean, compiled using data available through the National Oceanographic Data Center. This compilation clearly shows the general pattern of phosphate depletion in surface waters due to biological uptake (except in upwelling and high-latitude regions), and increased concentrations with depth due to regeneration from sinking organic matter. Conkright *et al.* (2000) present a similar compilation, taking into account seasonal variability. A clear limitation of these sorts of global compilations are the unavoidable data gaps that exist due to incomplete sampling coverage by oceanographic surveys. For surface waters, which are of interest because of the link between surface phosphate concentration, biological productivity, and the carbon cycle, this problem rapidly becomes insurmountable because of the high degree of variability on seasonal, and shorter, timescales.

With the advent of satellite remote sensing of surface seawater properties, attempts are now being made to use remotely sensed parameters to estimate surface-ocean nutrient (including phosphate) concentrations and distributions. This approach, although it has its own set of limitations, is one that can potentially redress the “data-gap” problem of oceanographic surveys. As a

recent example, Kamykowski *et al.* (2002) used the relationship between sea surface temperature and nutrient concentrations to generate date-specific estimates of nutrient levels in the world ocean. They use a derived parameter termed the “nutrient depletion temperature,” defined as the temperature above which nutrients are analytically undetectable, to estimate multinutrient availability in the world ocean. The output of this analysis was then linked to satellite-derived chlorophyll-*a* distributions to infer phytoplankton cell-size and taxonomic composition, with the aim of evaluating the impact of available nutrient (phosphate, nitrate, silicate, and iron) levels on phytoplankton community structure. There are other similar approaches being developed (see Kamykowski *et al.*, 2002 for citations), with the overall goal of determining global biogeochemical cycling of phosphate and other bioactive elements, and their impact on the global carbon cycle.

Dissolved organic phosphorus (DOP). Despite early studies indicating the importance of dissolved organic phosphorus (DOP) as a phosphorus source to marine primary producers (e.g., Redfield *et al.*, 1937; Ketchum *et al.*, 1955; Butler *et al.*, 1979; Jackson and Williams, 1985; Rivkin and Swift, 1985; Orrett and Karl, 1987), until recently many assessments of nutrient inventories and phytoplankton nutrition have ignored dissolved organic nutrient reservoirs. Two factors account for past lack of routine DOP data collection: (i) an historical bias in oceanographic nutrient studies favoring nitrogen as the limiting nutrient (e.g., Hecky and Kilham, 1988), relegating phosphate to a role of lesser importance, and (ii) the absence of a widely accepted, quick and convenient method of DOP measurement. Since the 1990s, there has been a growing appreciation of DOP as a significant player in phytoplankton nutrition (e.g., Björkman and Karl, 2003; Wu *et al.*, 2000; Abell *et al.*, 2000; Loh and Bauer, 2000; Monaghan and Ruttenberg, 1999). Accompanying this renewed interest, there have been a number of re-evaluations and improvements in analytical methods (e.g., Karl and Tien, 1992; Thomson-Bulldis and Karl, 1998; Monaghan and Ruttenberg, 1999). This section begins with a brief overview on current methods and recent method developments, followed by a sampling of recent work, highlighting unresolved research questions (see Karl and Bjorkman (2002) for a recent, comprehensive review of DOP, including an historical perspective).

Most available methods determine DOP as the difference between total dissolved phosphorus (TDP) and DIP, where TDP and DIP are quantified on separate splits of a single sample of filtered seawater. DIP is that portion of dissolved phosphorus that readily forms the

phosphomolybdate blue complex (e.g., Koroleff, 1983). This operationally defined fraction is sometimes referred to as “soluble reactive phosphorus (SRP),” since it is suspected that some easily hydrolysable DOP compounds may be converted to orthophosphate upon contact with the acidic colorimetric reagents (e.g., Rigler, 1968; Hudson *et al.*, 2000), although experimental acid hydrolysis studies of standard DOP compounds suggest that this effect may be small for many DOP compounds (Monaghan and Ruttenberg, 1999; however, see Baldwin, 1998). TDP is determined on a second split of filtered sample after oxidation/hydrolysis, which converts combined forms of dissolved phosphorus (DOP, polyphosphate) to orthophosphate. Concentration is then determined colorimetrically, as for DIP. Three oxidation/hydrolysis methods have been commonly used: high-temperature combustion/acid hydrolysis, persulfate oxidation, and UV oxidation. Although persulfate oxidation appears to be the most widely used method, Monaghan and Ruttenberg (1999) report inefficient recovery of phospholipids by this method and prefer the high-temperature combustion/hydrolysis method, which has the highest TDP recoveries of all DOP compound classes. In 1990, Ridal and Moore found that UV-oxidation showed poor recovery of nucleotide polyphosphates, and suggest combining the UV- and persulfate-oxidation methods for more complete DOP recovery (for recent reviews of TDP methods see Monaghan and Ruttenberg, 1999, Karl and Björkman, 2002, Mitchell and Baldwin, 2003). Aside from questions about the operationally defined nature of DIP, and hence the accuracy of DIP and DOP concentration determinations, another feature that plagues efforts to quantify DOP is the fact that it is a product of a “difference” method. When TDP and DIP concentrations are similar, a common occurrence in natural waters, and thus DOP is obtained by subtracting two similar numbers, the associated error can be quite large. This is not an uncommon problem in geochemistry, a field often limited by analytical capabilities, where the so-called “difference methods” are quite common.

The MAGIC (magnesium induced co-precipitation) method (Karl and Tien, 1992; Thomson-Bulldis and Karl, 1998) is currently finding wide usage in studies of dissolved phosphorus cycling in surface waters of oligotrophic oceanic regions, where dissolved phosphorus can be at or below detection limits of standard methods. This method calls for adding base to seawater, inducing precipitation of brucite ($\text{Mg}(\text{OH})_2$), which effectively strips out dissolved phosphorus via co-precipitation. The $\text{Mg}(\text{OH})_2$ pellet is retrieved after centrifugation, and redissolved for colorimetric phosphate determination of

DIP. As with the previously described difference methods, a pellet from a separate split is subjected to oxidation/hydrolysis for determination of TDP, and DOP is derived by difference. This method has also been adapted for use in concentrating DOP for isotopic studies of phosphate oxygen in seawater (see Section 8.13.3.3.3; Colman, 2002).

DOP can make up a significant fraction of the total dissolved phosphorus (TDP) pool in surface waters, in some cases seasonally surpassing levels of DIP (Butler *et al.*, 1979; Orrett and Karl, 1987; Cotner *et al.*, 1987; Karl and Tien, 1997). Karl and Björkman (2002) have compiled data from 23 studies from a variety of geographic locations, and report that marine DOP concentrations range from undetectable to as high as 99% of TDP. This compilation indicates that concentrations are highest in surface waters (37–99%TDP), while the lowest concentrations are observed at depth. In view of the extremely high proportions of DOP that can occur in marine surface waters, the locus of phytoplanktonic photosynthesis, a convincing case can be made for the importance of evaluating DOP bioavailability to marine primary producers.

The DOP pool includes phosphate esters (C–O–P bonded compounds, both mono- and diesters), phosphonates (C–P bonded compounds), and P associated with HMW organic matter, such as humic and fulvic acids (Table 7). Most DOP compounds are not available for direct uptake by phytoplankton or bacteria (e.g., Cembella *et al.*, 1984a,b). DOP can be rendered bioavailable by enzymatic hydrolytic production of orthophosphate, a form that can be directly assimilated (Ammerman, 1991). The question of bioavailability is essential for evaluating coupled C–N–P cycling and associated issues such as nutrient limitation, coupled ocean–atmosphere CO_2 dynamics, and climate change (through the nutrient– CO_2 connection, see Section 8.13.3.4.2), and coupled ocean–atmosphere O_2 dynamics (through the O_2 –Fe–P–C connection, see Section 8.13.3.4.2). The fact that different DOP compounds display variable enzyme susceptibility, and will therefore be of variable ecological significance, is the primary driving force behind studies of DOP composition in seawater. Studies on the molecular composition of DOP are, however, even less numerous than those on the bulk DOP pool. The paucity of information on DOP in natural waters is due again to analytical difficulties associated with analyzing low DOP levels that are typical of natural waters, a factor that is exacerbated in seawater where any measurements must be made against the background of a complex salt matrix. The situation of analytical roadblocks to detailed study of DOP molecular composition is not dissimilar to that described for solid-phase organic phosphorus (see Section 8.13.3.3.2). A number of approaches are

Table 7 Selected organic phosphorus compounds identified or likely to be present in seawater.

| Compound | Chemical formula (molecular weight) | P (% by weight) | Molar C : N : P |
|---|--|--------------------|-----------------|
| <i>Monophosphate esters</i> | | | |
| Ribose-5-phosphoric acid (R-5-P) | C ₅ H ₁₁ O ₈ P (230.12) | 13.5 | 5:_:1 |
| Phospho(enol)pyruvic acid (PEP) | C ₃ H ₅ O ₆ P (168) | 18.5 | 3:_:1 |
| Glyceraldehyde 3-phosphoric acid (G-3-P) | C ₃ H ₇ O ₆ P (170.1) | 18.2 | 3:_:1 |
| Glycerphosphoric acid (gly-3-P) | C ₃ H ₉ O ₆ P (172.1) | 18.0 | 3:_:1 |
| Creatine phosphoric acid (CP) | C ₄ H ₁₀ N ₃ O ₅ P (211.1) | 14.7 | 4:3:1 |
| Glucose-6-phosphoric acid (glu-6-P) | C ₆ H ₁₃ O ₉ P (260.14) | 11.9 | 6:_:1 |
| Ribulose-1,5-bisphosphoric acid (RuBP) | C ₅ H ₆ O ₁₁ P ₂ (304) | 20.4 | 2.5:_:1 |
| Fructose-1,6-diphosphoric acid (F-1,6-DP) | C ₆ H ₁₄ O ₁₂ P ₂ (340.1) | 18.2 | 3:_:1 |
| Phosphoserine (PS) | C ₃ H ₈ NO ₆ P (185.1) | 16.7 | 3:1:1 |
| <i>Nucleotides and derivatives</i> | | | |
| Adenosine 5'-triphosphoric acid (ATP) | C ₁₀ H ₁₆ N ₅ O ₁₃ P ₃ (507.2) | 18.3 | 3.3:1.7:1 |
| Uridylic acid (UMP) | C ₉ H ₁₃ N ₂ O ₉ P (324.19) | 9.6 | 9:2:1 |
| Uridine-diphosphate-glucose (UDPG) | C ₁₅ H ₂₄ N ₂ O ₁₇ P ₂ (566.3) | 10.9 | 7.5:1:1 |
| Guanosine 5'-diphosphate-3'-diphosphate (ppGpp) | C ₁₀ H ₁₇ N ₅ O ₁₇ P ₄ (603) | 20.6 | 2.5:1.5:1 |
| Pyridoxal 5-monophosphoric acid (PyMP) | C ₈ H ₁₀ NO ₆ P (247.2) | 12.5 | 8:1:1 |
| Nicotinamide adenine dinucleotide phosphate (NADP) | C ₂₂ H ₂₈ N ₂ O ₁₄ N ₆ P ₂ (662) | 9.4 | 11:3:1 |
| Ribonucleic acid (RNA) | Variable | ~9.2 | ~9.5:4:1 |
| Deoxyribonucleic acid (DNA) | Variable | ~9.5 | ~10:4:1 |
| Inositolhexaphosphoric acid, or phytic acid (PA) | C ₆ H ₁₈ O ₂₄ P ₆ (660.1) | 28.2 | 1:_:1 |
| <i>Vitamins</i> | | | |
| Thiamine pyrophosphate (vitamin B ₁) | C ₁₂ H ₁₉ N ₄ O ₇ P ₂ S (425) | 14.6 | 6:2:1 |
| Riboflavin 5'-phosphate (vitamin B ₂ -P) | C ₁₇ H ₂₁ N ₄ O ₉ P (456.3) | 6.8 | 17:4:1 |
| Cyanocobalamin (vitamin B ₁₂) | C ₆₃ H ₈₈ CoN ₁₄ O ₁₄ P (1355.42) | 2.3 | 63:14:1 |
| <i>Phosphonates</i> | | | |
| Methylphosphonic acid (MPn) | CH ₃ O ₃ P (96) | 32.3 | 1:_:1 |
| Phosphonoformic acid (FPn) | CH ₃ O ₅ P (126) | 24.6 | 1:_:1 |
| 2-aminoethylphosphonic acid (2-AEPn) | C ₂ H ₈ NO ₄ P (141) | 22.0 | 2:1:1 |
| <i>Other compounds/compound classes</i> | | | |
| Marine fulvic acid (FA) ^a | Variable | 0.4–0.8 | 80–100:_:1 |
| Marine humic acid (HA) ^a | Variable | 0.1–0.2 | >300:_:1 |
| Phospholipids (PL) | Variable | ≤0.4 | ~40:1:1 |
| Malathion (Mal) | C ₉ H ₁₆ O ₅ PS (267) | 11.6 | 9:_:1 |
| “Redfield” phytoplankton | Variable | 1–3 | 106:16:1 |

After Karl and Björkman (2002).

^a Marine HA and FA are operationally defined fractions, and their composition may be variable (values are from Nissenbaum, 1979). Phosphate associated with HA and FA may be organically bound. Alternatively, it may be inorganic orthophosphate linked to HA and/or FA through metal bridges (Laarkamp, 2000).

currently in use to determine DOP composition and bioavailability, and have provided valuable insights.

³¹P-NMR spectroscopy applied to the HMW fraction of DOP, concentrated from seawater by ultrafiltration (Clark *et al.*, 1999; Kolowitz *et al.*, 2001), has revealed a striking uniformity in HMW-DOP composition at different geographical locations, regardless of water depth or proximity to shore. One unanticipated result of this work was the large proportion of phosphonates (~25%) present in HMW-DOP, the remainder being composed of phosphoesters. These authors hypothesize that the high proportion of phosphonates

result from selective preservation of these compounds over time, based on the assumption that phosphonates are less easily degradable than organophosphates (however, see discussion in Section 8.13.3.3.2). Another intriguing result of these ³¹P-NMR studies was the observation of a sixfold decrease in HMW-DOP concentration from surface to 4,000 m water depth in abyssal sites, with no indication of preferential mineralization of phosphoesters over phosphonates. The latter finding is apparently at odds with the initial hypothesis of preferential preservation of phosphonates in the HMW-DOP pool. Finally, Clark *et al.* (1998) note a shift in the molar C : N : P

ratios of the HMW-DOP pool with depth, shifting from 247C : 15N : 1P in surface waters, to 321 : 19 : 1 at 375 m, and finally to 539 : 30 : 1 at 4,000 m water depth, indicating preferential mineralization of phosphorus from HMW-DOP, relative to nitrogen and carbon. Several drawbacks to this methodology in its current state of development include: (i) the necessity of pre-concentration (typically by ultrafiltration) to meet detection limit constraints, with possible distortion of *in situ* composition resulting from pre-concentration treatments (e.g., Nanny and Minear, 1997; Bauer *et al.*, 1996); (ii) inaccessibility of lower-molecular-weight, possibly more bioavailable, DOP. The HMW (>1 nm) fraction of the DOP pool, which is amenable to pre-concentration via ultrafiltration and subsequent NMR analysis, represents only one-third of the total DOP pool; the other two-thirds of this pool, made up of smaller molecular weight DOP compounds, remain outside our window of current analytical accessibility. Despite these drawbacks, ³¹P-NMR is an exciting and promising tool for the study of DOP, and has provided insights that were not possible with previously available methods.

Other methods that have been used for DOP characterization are briefly summarized here (see Karl and Björkman (2002) for a more detailed discussion of these approaches, including case studies; see also review by Mitchell and Baldwin (2003)). Fractionation of DOP according to molecular weight, the most recent incarnation of which uses tangential flow ultrafiltration (e.g., Nanny *et al.*, 1994; Nanny and Minear, 1997), is often coupled to other diagnostic analytical methods, such as ³¹P-NMR (see above), or enzyme hydrolysis characterization (Suzumura *et al.*, 1998). Enzyme hydrolysis studies add specific enzymes to natural waters to achieve partial determination of its DOP composition (e.g., Kobori and Taga, 1979; McKelvie *et al.*, 1995; Suzumura *et al.*, 1998). This type of approach is also used to determine the potential bioavailability of the DOP pool (e.g., DeFlaun *et al.*, 1987). Karl and Yanagi (1997) utilized a partial photochemical oxidation technique to gain insights into the composition of oceanic DOP. A number of specific compounds have also been directly measured in seawater (Table 7) using a variety of methodologies, including nucleic acids, ATP and related nucleotides, phospholipids, and vitamins. As it is the quality of bioavailability that is of prime ecological significance, a number of studies have used radiophosphorus uptake studies to determine bioavailability of model DOP compounds (Björkman and Karl, 1994) and *in situ* marine DOP (Björkman *et al.*, 2000; Björkman and Karl, 2003; Bossard and Karl, 1986).

Water column C : P ratios. The concept of preferential regeneration of phosphorus relative to

carbon during respiration of organic matter in marine sediments (see Section 8.13.3.2) has also been applied to particulate (C : P)_{org} ratios in the marine water column. If it is true, as many sediment studies suggest, that phosphorus is preferentially regenerated during microbial respiration in the early diagenetic environment, it stands to reason that this process would have already begun in the water column. In a series of phytoplankton decomposition experiments, Grill and Richards (1976) demonstrated that phosphorus was regenerated preferentially to nitrogen. Consistent with these experimental findings, a number of sediment trap studies have observed increasing marine particulate (C : P)_{org} ratios with water column depth, to ratios elevated above the Redfield ratio (e.g., Copin-Montegut and Copin-Montegut, 1972; Knauer *et al.*, 1979; Liebezeit, 1991; Honjo and Manganini, 1993). Most of these studies did not account for the effect of mineralization during particulate storage in the sediment trap, and therefore could represent overestimates of the preferential phosphorus regeneration effect (Peng and Broecker, 1987; also discussed in Delaney, 1998 and Anderson *et al.*, 2001). However, Honjo and Manganini (1993) corrected particulate phosphorus concentrations for in-trap mineralization, and the trend of preferential P-mineralization was still observed. In line with these results for water column particulate matter, Clark *et al.* (1998) and Loh and Bauer (2000) have found evidence for preferential phosphorus regeneration (relative to nitrogen and carbon) in HMW- and bulk-DOP, respectively, in the form of increasing ratios with increasing water depth.

In direct contradiction to the suggestion of preferential phosphorus remineralization derived from water column particulates and DOP, outlined above, regression analyses of dissolved nutrient ratios along isopycnals do not find evidence for preferential regeneration of phosphorus relative to carbon in the water column (e.g., Peng and Broecker, 1987). Anderson and Sarmiento concluded that organic matter flux to the sediment water interface must be dominated by “fast-flux particles,” such as fecal pellets, and must not differ substantially from the near-Redfield remineralization ratios observed in their isopycnal analysis. They go on to caution that their results may not be applicable to high-latitude regions, to the ocean above 400 m (the upper depth limit of their analysis), or to short time- or length-scales. This disclaimer is significant, given that most organic matter in the modern ocean is buried in relatively shallow, continental margin sediments (Berner, 1982). It is also important to note that each of the studies using hydrographic data to model C : N : P ratios have imbedded in them a series of assumptions, and different approaches can lead to different results. For example, Thomas (2002) conducts a

regression analysis that indicates increasing C : P ratios with water depth in the North Atlantic, consistent with sediment trap data (Honjo and Manganini, 1993), but in disagreement with other regression analysis studies. The discrepancies that exist between studies of modeled versus measured C : P ratios indicate that we have not yet arrived at the “truth” about the extent of preferential P-mineralization of sinking organic matter in the marine water column. Reconciling these conflicting lines of argument is an important priority for achieving accurate coupled models of carbon, nitrogen, and phosphorus.

Cosmogenic ^{32}P and ^{33}P as tracers of phosphorus cycling in surface waters. There are two radioactive isotopes of phosphorus, ^{32}P (half-life = 14.3 d) and ^{33}P (half-life = 25.3 d). Both have been widely used in the study of biologically mediated phosphorus cycling in aquatic systems. Until very recently, these experiments have been conducted by artificially introducing radiophosphorus into laboratory incubations, or far more rarely, by direct introduction into natural waters under controlled circumstances. Such experiments necessarily involve significant perturbation of the system, which can complicate interpretation of results. Recent advances in phosphorus sampling and radioisotope measurement have made it possible to use naturally produced ^{32}P and ^{33}P as *in situ* tracers of phosphorus cycling in surface waters (Lal and Lee, 1988; Lee *et al.*, 1991; Waser and Bacon, 1995; Waser *et al.*, 1996; Benitez-Nelson and Buesseler, 1998, 1999; Benitez-Nelson and Karl, 2002). These advances have permitted studies of net P-recycling in the absence of experimental perturbation caused by addition of artificially introduced radiophosphorus.

^{32}P and ^{33}P are naturally produced in the atmosphere by cosmic ray interactions with atmospheric argon nuclei. They are then quickly scavenged onto aerosol particles, and delivered to the ocean surface predominantly in rain. The ratio of $^{33}\text{P}/^{32}\text{P}$ introduced to the oceans by rainfall remains relatively constant, despite the fact that absolute concentrations can vary from one precipitation event to another. Once the dissolved phosphorus is incorporated into a given surface water phosphorus pool (e.g., uptake by phytoplankton or bacteria, grazing of phytoplankton or bacteria by zooplankton, or abiotic sorption), the $^{33}\text{P}/^{32}\text{P}$ ratio will increase in a systematic way as a given pool ages. This increase in the $^{33}\text{P}/^{32}\text{P}$ ratio with time results from the different half-lives of the two phosphorus radioisotopes. By measuring the $^{33}\text{P}/^{32}\text{P}$ ratio in rain and in different marine phosphorus pools (e.g., DIP, DOP (sometimes called soluble nonreactive phosphorus, or SNP), particulate-P of various size classes corresponding to different levels in the food chain), the net age of phosphorus in any of these reservoirs can be determined (Table 8). New insights into P-cycling in oceanic surface waters derived from recent work using the cosmogenically produced $^{33}\text{P}/^{32}\text{P}$ ratio include (refer to citations in Table 8): (i) turnover rates of DIP in coastal and oligotrophic oceanic surface waters range from 1 d to 20 d; (ii) variable turnover rates in the DOP pool range from <1 week to >100 d, suggesting differences in either the demand for DOP, or the lability of DOP toward enzymatic breakdown; (iii) in the Gulf of Maine, DOP turnover times vary seasonally, increasing from 28 d in July to >100 d in August, suggesting that the DOP pool may evolve compositionally during the growing seasons; (iv) highly variable TDP residence times

Table 8 Turnover rates of $^{\text{a}}$ DIP and $^{\text{b}}$ DOP in surface seawater.

| Phosphorus pool | P turnover rate | | |
|--|--|-----------------|-----------------------------------|
| | Coastal | Open ocean | References |
| DIP | <1 h to 10 d (>1,000 d in Bedford Basin) | Weeks to months | 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 |
| Total DOP | 3 d to >90 d | 20–300 d | 10, 11, 12, 13, 14, 15, 16, 22 |
| Bioavailable DOP (model compounds) | 2–30 d | 1–4 d | 9, 17, 18, 19 |
| Microplankton (<1 μm) | >1–3 d | NA | 11 |
| Phytoplankton (>1 μm) | <1–8 d | <1 week | 11, 20 |
| Macrozooplankton (>280 μm) | 14–40 d | 30–80 d | 11, 14, 15, 20, 21 |

After Benitez-Nelson (2000).

References: (1) Pomeroy (1960); (2) Duerden (1973); (3) Taft *et al.* (1975); (4) Harrison *et al.* (1977); (5) Perry and Eppley (1981); (6) Smith *et al.* (1985); (7) Sorokin (1985); (8) Harrison and Harris (1986); (9) Björkman and Karl (1994); (10) Björkman *et al.* (2000); (11) Benitez-Nelson and Buesseler (1999); (12) Jackson and Williams (1985); (13) Orrett and Karl (1987); (14) Lal and Lee (1988); (15) Lee *et al.* (1992); (16) Karl and Yanagi (1997); (17) Ammerman and Azam (1985); (18) Nawrocki and Karl (1989); (19) Björkman and Karl (2001); (20) Waser *et al.* (1996); (21) Lee *et al.* (1991); (22) Benitez-Nelson and Karl (2002).

$^{\text{a}}$ DIP is equivalent to the soluble reactive P (SRP) pool, which may include some phosphate derived from hydrolysis of DOP (e.g., see Monaghan, and Ruttenberg, 1998). $^{\text{b}}$ DOP is equivalent to the soluble nonreactive P (SNP) pool which may include dissolved inorganic polyphosphates (e.g., see Karl and Yanagi, 1997).

in the North Pacific Subtropical Gyre suggest dynamic phosphorus utilization over short timescales of weeks to months, and correlation of apparent TDP ages with C-fixation rates suggests preferential removal of younger, presumably more labile TDP; (v) comparison of the $^{33}\text{P}/^{32}\text{P}$ ratio in different particulate size classes indicates that the age of phosphorus generally increases at successive levels in the food chain; and (vi) under some circumstances, the $^{33}\text{P}/^{32}\text{P}$ ratio can reveal which dissolved pool is being ingested by a particular size class of organisms. Utilization of this new tool highlights the dynamic nature of P-cycling in surface waters by revealing the rapid rates and temporal variability of P-turnover. It further stands to provide new insights into ecosystem nutrient dynamics by revealing, for example, that (i) low phosphorus concentrations can support high primary productivity through rapid turnover rates, and (ii) there is preferential utilization of particular dissolved phosphorus pools by certain classes of organisms.

Oxygen isotopes of phosphate in seawater. Use of the oxygen isotopic composition of phosphate in biogenic hydroxyapatite (bones, teeth) as a paleotemperature and climate indicator was pioneered by Longinelli (1966), and has since been fairly widely and successfully applied (Kolodny *et al.*, 1983; Shemesh *et al.*, 1983; Luz *et al.*, 1984). The relationship between phosphate oxygen isotopic fractionation and temperature originally proposed (Longinelli and Nuti, 1973) has been confirmed by later work (Blake *et al.*, 1997; Colman, 2002).

Phosphorus has only one stable isotope (^{31}P) and occurs almost exclusively as orthophosphate (PO_4) under Earth surface conditions. The phosphorus-oxygen bond in phosphate is highly resistant to nonenzymatic oxygen isotope exchange reactions, but when phosphate is metabolized by living organisms, that is, when organic phosphorus compounds are first biosynthesized and subsequently enzymatically hydrolyzed in the intracellular environment, oxygen isotopic exchange is rapid and extensive (Blake *et al.*, 1997, 1998; Paytan *et al.*, 2002). Such exchange results in temperature-dependent fractionations between phosphate and ambient water (Colman, 2002). This property renders phosphate oxygen isotopes useful as indicators of present or past metabolic activity of organisms, and allows distinction of biotic from abiotic processes operating in the cycling of phosphorus through the environment.

New methods for the isolation and purification of inorganic phosphate (P_i) from natural waters (Colman *et al.*, 2000; Colman, 2002) have permitted phosphate-oxygen isotopic ($\delta^{18}\text{O}-\text{P}_i$) analysis of dissolved seawater inorganic phosphate as a tracer of phosphate source, water mass mixing,

and biological productivity (Colman, 2002). In this study, Colman (2002) demonstrates that microbial phosphate cycling imprints the $\delta^{18}\text{O}-\text{P}_i$ signature of major aquatic phosphate reservoirs. For example, on the basis of residence time constraints, Colman (2002) demonstrates that microbial cycling of P_i in Long Island Sound (USA) estuary is rapid enough to overprint, on a time scale of weeks, the distinctly different $\delta^{18}\text{O}-\text{P}_i$ value of the major water source to the estuary (Connecticut River). Biological P_i turnover appears to keep pace with significant temperature shifts (3–9°C cooling) experienced by Long Island Sound surface waters during the study period, leading Colman (2002) to conclude that turnover rates could be even more rapid than implied on the basis of residence time constraints alone. This observation is particularly interesting, given that Long Island Sound is generally considered to be strongly nitrogen limited (Colman, 2002).

Another example of insights gained into microbial P_i cycling through application of $\delta^{18}\text{O}-\text{P}_i$ analysis derives from the observation (Colman, 2002) that deepwater ocean samples from two oligotrophic oceanic regions (the Subtropical North Pacific Gyre, and the Sargasso Sea in the North Atlantic) are offset from equilibrium values. The direction of offset (to lower values) implies that some fraction of the P_i reservoir at depth is regenerated extracellularly from sinking particulate organic matter, resulting in only partial equilibration of the regenerated P_i flux (Colman, 2002).

The $\delta^{18}\text{O}-\text{P}_i$ system has also recently been applied to phosphates associated with ferric iron oxyhydroxide precipitates in submarine ocean ridge sediments (Blake *et al.*, 2000, 2001). The $\delta^{18}\text{O}-\text{P}_i$ signature of phosphate associated with these authigenic Fe-oxyhydroxide precipitates indicates microbial phosphate turnover at elevated temperatures. The latter observation suggests that phosphate oxygen isotopes may be useful biomarkers for fossil hydrothermal vent systems. On the basis of this work, Blake *et al.* (2001) also hypothesize that authigenic phases extant on other planets may retain imprints of primitive biospheres, in the form of detectable and diagnostic $\delta^{18}\text{O}-\text{P}_i$ composition, imparted by biochemical, enzymatic processes.

8.13.3.3.4 Phosphorus limitation of marine primary photosynthetic production

In terrestrial soils and in the euphotic zone of lakes and the ocean the concentration of dissolved orthophosphate is typically low. When bioavailable phosphorus is exhausted prior to

more abundant nutrients, it limits the amount of sustainable biological productivity. This is the ecological principle often referred to as Liebig's (1840) Law of the Minimum, first established for terrestrial plants and then adapted to phytoplankton growth (Blackman, 1905), in which the standing phytoplankton stock is limited by the substance least available relative to the amount required for synthesis of healthy biomass. Phosphorus limitation in lakes is widely accepted (e.g., Hecky and Kilham, 1988), and terrestrial ecosystems are often phosphorus-limited (e.g., Lajtha and Harrison, 1995; Chadwick *et al.*, 1999). In the oceans, however, phosphorus limitation is the subject of controversy and debate (e.g., Smith, 1984; Hecky and Kilham, 1988; Codispoti, 1989; Falkowski, 1997; Palenik and Dyhrman, 1998).

The prevailing paradigm among geochemists is that phosphorus is most probably the limiting nutrient on long, geologic time-scales (e.g., Redfield, 1958; Holland, 1978; Broecker and Peng, 1982; Smith and Mackenzie, 1987; Kump, 1988). According to this paradigm, while there is an abundant reservoir of nitrogen (gaseous N_2) in the atmosphere that can be rendered bioavailable by N-fixing photosynthetic organisms, phosphorus supply to the ocean is limited to that weathered off the continents and delivered by rivers, with some minor atmospheric input. As a consequence of continental weathering control on phosphorus supply to the oceans (and ultimately, tectonic control, see Section 8.13.3.4.1) phosphorus availability limits net primary production on geological timescales (however, see Codispoti (1989), Falkowski (1997), and Lenton and Watson (2000), for counter-arguments that favor nitrogen limitation).

In the modern ocean, in contrast, the prevailing view has been that nitrogen, and not phosphorus, is the limiting nutrient for marine primary productivity (Codispoti, 1989; Tyrrell, 1999). This paradigm was replaced in the 1970s, largely due to the work of Ryther and Dunstan (1971), who showed that nitrate stimulated phytoplankton growth off the coast of Long Island, NY, whereas phosphate did not. This view has been widely supported by studies using large oceanographic data sets (e.g., GEOSECS, TTO, WOCE), which show that when nitrate and phosphate concentrations are plotted against one another for the world's oceans, nitrate drops to undetectable limits first, with residual phosphate present; or alternatively that the nitrate: phosphate ratio for much of the world's oceans is equal to or slightly lower than the Redfield ratio (e.g., Tyrrell and Law, 1997; Tyrrell, 1999).

Several factors not considered by the N-limitation paradigm have been receiving attention recently. For example, the recognition that phytoplankton can utilize dissolved organic nutrients, both phosphorus (DOP) and nitrogen, render

questionable any conclusions drawn on the basis of inorganic nutrients alone (e.g., Jackson and Williams, 1985; Karl *et al.*, 1997; Palenik and Dyhrman, 1998; Karl and Björkman, 2002). Further, there is a growing appreciation for the heterogeneity of the ocean, with different regions potentially experiencing different limiting nutrient conditions (e.g., Palenik and Dyhrman, 1998), sometimes variable on decadal (e.g., Karl, 1999) or shorter timescales (e.g., Monaghan and Ruttenberg, 1999; Dyhrman and Palenik, 1999). Consideration of these and other factors suggest that the nutrient limitation debate has been too simplistic.

The dearth of studies on marine phosphorus biogeochemistry prior to the early 1980s can in part be explained by the entrenched view of marine scientists that phosphorus was the "lesser important" of the essential nutrients, since nitrogen and not phosphorus was considered to be the limiting nutrient. This view is currently being challenged in a number of different venues, by a number of different scientists, and a growing consensus is emerging that P-limitation may be important not just on geologic time scales, but in the modern ocean, as well. The remainder of this section highlights the growing body of literature that present evidence for phosphorus limitation of primary productivity in some marine systems.

In the oligotrophic gyres of both the western North Atlantic and subtropical North Pacific, evidence in the form of dissolved N : P ratios has been used to argue convincingly that these systems are currently P-limited (e.g., Ammerman *et al.*, 2003; Cavender-Barres *et al.*, 2001; Karl *et al.*, 2001; Wu *et al.*, 2000). The N : P ratio of phytoplankton under nutrient sufficient conditions is 16N : 1P (the Redfield ratio). A positive deviation from this ratio indicates probable phosphorus limitation, while a negative deviation indicates probable nitrogen limitation. In the North Pacific at the Hawaiian Ocean Time Series (HOT) site, there has been a shift since the 1988 inception of the time series to N : P ratios exceeding the Redfield ratio in both particulate and surface ocean dissolved nitrogen and phosphorus (Figure 15). Coincident with this shift has been an increase in the prevalence of the N-fixing cyanobacterium *Trichodesmium* (Table 9). Currently, it appears that the supply of new nitrogen has shifted from a limiting flux of upwelled nitrate from below the euphotic zone to an unlimited pool of atmospheric N_2 rendered bioavailable by the action of nitrogen-fixers. This shift is believed to result from climatic changes that promote water column stratification, a condition that selects for N_2 -fixing microorganisms, thus driving the system to P-limitation. A similar situation exists in the subtropical Sargasso Sea at the Bermuda OceanTime Series (BATS) site,

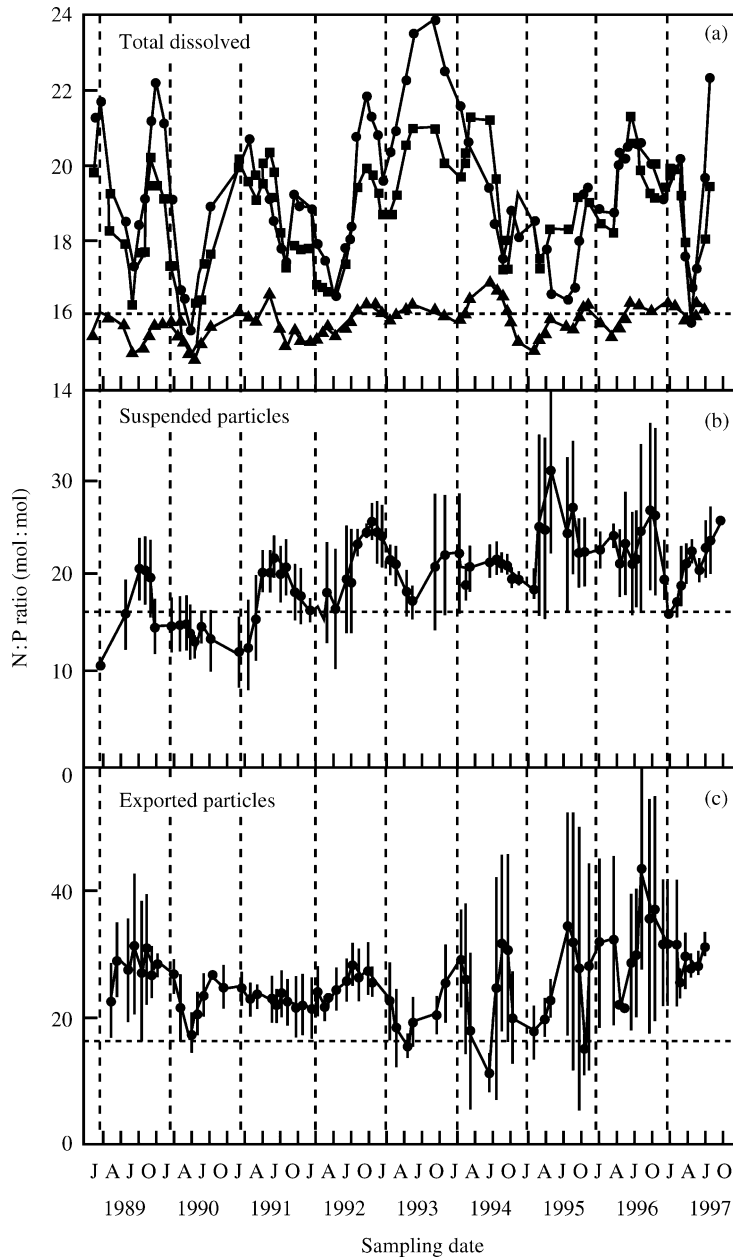


Figure 15 Time-series molar N : P ratios in (a) the dissolved pool, (b) suspended particulate matter, and (c) exported particulate matter from the HOT time-series site at station ALOHA in the subtropical North Pacific near Hawaii. Panel (a) shows the three-point running mean N : P ratios for 0–100 m (circles), 100–200 m (squares), and 200–500 m (triangles). Panel (b) shows the three-point running mean (± 1 SD) for the average suspended particulate matter in the upper water column (0–100 m). Panel (c) shows the three-point running mean (± 1 SD) for the average N : P ratio of sediment trap-collected particulate matter at 150 m. The Redfield ratio (N : P = 16) is represented by a dashed line in all three panels. Particulate and upper water column dissolved pools show an increasing N : P ratio throughout the time-series, with a preponderance of values in excess of the Redfield ratio (after [Karl *et al.*, 1997](#)).

where currently the dissolved phosphorus concentrations (especially DIP) are significantly lower than at the HOT site, indicating even more severe P-limitation ([Table 9](#); see also [Ammerman *et al.*, 2003](#)).

A number of coastal systems also display evidence of P-limitation, sometimes shifting

seasonally from nitrogen to phosphorus limitation in concert with changes in environmental features such as upwelling and river runoff. On the Louisiana Shelf in the Gulf of Mexico ([MacRae *et al.*, 1994](#); [Pakulski *et al.*, 2000](#)), the Eel River Shelf of northern California (USA) ([Monaghan and Ruttenberg, 1999](#)), the upper Chesapeake Bay

Table 9 Parameters affecting nutrient limitation: comparison between North Atlantic and North Pacific gyres.

| Parameter | Sargasso Sea | Pacific HOT site |
|--|--------------------------|-------------------------|
| DIP (nM) | 0.48 ± 0.27 ^a | 9–40 ^b |
| TDN (nM) | 4512 ± 430 | 5680 ± 620 ^b |
| TDP (nM) | 75 ± 42 | 222 ± 14 ^b |
| TDN:TDP | 60 ± 7 | 26 ± 3 ^b |
| N ₂ -fixation rate (mmol N m ⁻² yr ⁻¹) | 72 ^c | 31–51 ^c |

After Wu *et al.* (2000).

^a Average DIP between 26° and 31° N in Sargasso Sea surface waters in March 1998. ^b North Pacific near Hawaii at station ALOHA (the HOT site) during 1991–1997. ^c See Wu *et al.* (2000) for method of calculation or measurement.

(USA) (Fisher *et al.*, 1992; Malone *et al.*, 1996), and regions of the Baltic Sea (Granéli *et al.*, 1990) surface water column dissolved inorganic N : P ratios indicate seasonal phosphorus limitation. The suggestion of P-limitation is reinforced in the Louisiana and Eel River Shelf studies by the occurrence of alkaline phosphatase activity (MacRae *et al.*, 1994; Monaghan and Ruttenberg, 1999), an enzyme induced only under conditions of physiologically stressful low phosphate concentrations that can be P-limiting (e.g., Ammerman, 1991; Dyhrman and Palenik, 1999). Alkaline phosphatase has also been observed seasonally in Narragansett Bay (Dyhrman and Palenik, 1999). In this latter study, a novel probe was utilized that permits evaluation of phytoplankton P physiology at the single-cell level, by fluorescently labeling the site of alkaline phosphatase activity (see Section 8.13.3.2.1, discussion of the ELF® probe). Although these coastal sites are recipients of anthropogenically-derived nutrients (N and P) that stimulate primary productivity above ‘natural’ levels, the processes that result in shifts in the limiting nutrient are not necessarily related to anthropogenic effects. Some other oceanic sites where P limitation of primary productivity has been documented include the Mediterranean Sea (Krom *et al.*, 1991), Florida Bay (USA) (Fourqurean *et al.*, 1993), Northeastern Gulf of Mexico (Myers and Iverson, 1981); the Chesapeake Bay (Fisher *et al.*, 1992, 1995; Malone *et al.*, 1996) Shark Bay (Australia) (Smith and Atkinson, 1984), Trondheims fjord, Norway (Myklestad and Sakshaug, 1983) and Oslofjord, Norway (Paasche and Erga, 1988), the Baltic Sea (Granéli *et al.*, 1990).

One key question that studies of N- and P-limitation must address before meaningful conclusions may be drawn about P- versus N-limitation of marine primary productivity, is the extent to which the dissolved organic nutrient pools are accessible to phytoplankton. In brief, this is the question of bioavailability. Many

studies of nutrient cycling and nutrient limitation do not include measurement of these quantitatively important nutrient pools (e.g., Downing, 1997), even though there is indisputable evidence that some portion of the DOP and DON pools are bioavailable (e.g., Rivkin and Swift, 1980; Björkman and Karl, 1994; Karl and Björkman, 2002). Dissolved inorganic N : P ratios and the presence of alkaline phosphatase (APase) activity are two common diagnostic parameters for inferring P-limitation in field studies. The occurrence of high N : P ratios and APase activity imply that phytoplankton are stressed by low DIP levels. It is important to note that P-stress will progress to P-limitation only if the phytoplankton physiological response to P-stress, e.g., synthesis of APase, fails to relieve the P-stress. Progression to P-limitation thus is linked to DOP bioavailability. An important direction for future research is to characterize the DOP (and DON) pools at the molecular level, and to evaluate what fraction of these are bioavailable. The analytical challenge of identifying the molecular composition of the DOP pool is significant. As discussed in Section 8.13.3.3.3, recent advances in ³¹P-NMR spectroscopy have permitted a first look at the high molecular weight (>1 nm) fraction of the DOP pool, but smaller, possibly more bioavailable DOP compounds remain outside the window of current analytical accessibility.

8.13.3.3.5 The oceanic residence time of phosphorus

As phosphorus is considered the most likely limiting nutrient on geologic timescales (e.g., Redfield, 1958; Broecker and Peng, 1982; Holland, 1978, 1984; Smith, 1984; Howarth *et al.*, 1995; see Section 8.13.3.3.4), an accurate determination of its oceanic residence time is crucial to understanding how levels of primary productivity may have varied in the Earth’s past. Residence time provides a means of evaluating how rapidly the oceanic phosphorus inventory may have changed in response to variations in either input (e.g., continental weathering, dust flux) or output (e.g., burial with sediments). In its role as limiting nutrient, phosphorus will dictate the amount of surface–ocean net primary productivity, and hence atmospheric CO₂ draw-down that will occur by photosynthetic biomass production. It has been suggested that this so-called “nutrient–CO₂” connection may link the oceanic phosphorus cycle to climate change due to reductions or increases in the atmospheric greenhouse gas inventory (Broecker, 1982a,b; Boyle, 1990; see Section 8.13.3.4.2). Oceanic phosphorus residence time and response time (the inverse of residence

time) will dictate the timescales over which such a P-induced climate effect may operate.

Since the 1990s there have been several re-evaluations of the marine phosphorus cycle in the literature, reflecting changes in our understanding of the identities and magnitudes of important P-sources and P-sinks. Newly identified marine P-sinks include disseminated authigenic carbonate fluorapatite (CFA) in sediments in nonupwelling environments (see Section 8.13.3.3.2), authigenic (REE)-aluminophosphates in sandstones (Rasmussen, 2000; Section 8.13.3.3.2), and hydrothermal P-scavenging via basalt–seawater interaction on ridge-flanks of MOR systems (Wheat *et al.*, 1996; Section 8.13.3.3.2). Continental margins in general are quantitatively important sinks for organic and ferric iron-bound phosphorus, as well. When newly calculated P-burial fluxes in continental margins, including the newly identified CFA and aluminophosphate phosphorus (dominantly Al-REE-P) sinks are combined with older estimates of P-burial fluxes in the deep sea, the overall burial flux results in a much shorter residence time than the canonical value of 100 kyr found in most text books (Table 3). This shorter residence time suggests that the oceanic P-cycle is subject to perturbations on shorter timescales than has previously been believed.

The revised, larger burial flux cannot be balanced by the dissolved riverine input alone. However, when the fraction of riverine particulate-P that is believed to be released upon entering the marine realm is taken into account, the possibility of a balance between inputs and outputs becomes more feasible. Residence times estimated on the basis of P-inputs that include this “releasable” riverine particulate-P fall within the range of residence time estimates derived from P-burial fluxes (Table 3). Despite the large uncertainties associated with these numbers, as evidenced by the maximum and minimum values derived from both input and removal fluxes, these updated residence times are all significantly shorter than the canonical value of 100 kyr. Residence times on the order of 10–17 kyr make P-perturbations of the ocean–atmosphere CO₂ reservoir on the timescale of glacial–interglacial climate change feasible. It is interesting to speculate about the fate of P sequestered in continental margin sediments during high sea level stands once sea level drops, as it does during glacial times. As the phosphorus in margin sediments becomes subjected to subaerial weathering and erosion as sea level lowers, if it is remobilized in bioavailable forms, it could augment productivity-driven CO₂ draw-down and enhance glacial cooling trends (Compton *et al.*, 1993; Ruttenger, 1993).

8.13.3.4 Phosphorus Cycling Over Long, Geologic Timescales

8.13.3.4.1 *The role of tectonics in the global phosphorus cycle*

Given the well-studied role of tectonics in carbon cycling on timescales of tens to hundreds of millions of years (e.g., Berner *et al.*, 1983), it has recently been recognized that, owing to the linkage of carbon and phosphorus cycles through photosynthetic uptake (see discussion in Sections 8.13.2.3 and 8.13.3.3.2), tectonics likely play an important role in the global phosphorus cycle over these long timescales, as well (Guidry *et al.*, 2000). In this formulation, the balance between subduction of phosphorus bound up in marine sediments and underlying crust, and creation of new crystalline rock, sets the mass of exogenic phosphorus.

In brief, P-delivery rate to the ocean is controlled by continental weathering. Unlike carbon and nitrogen, there is no gaseous phosphorus phase of any importance to supplement the continental weathering flux. (Note that the reduced phosphorus gas phosphine (PH₃) has been found in trace quantities in highly reducing media (Dévai *et al.*, 1988; Gassman, 1994), but is an insignificant reservoir at current Earth surface conditions (Burford and Bremner, 1972; Schink and Friedrich, 2000), unless it is a more important component of reduced volcanic gases that has been recognized.) P-removal rate from the ocean is controlled by burial with sediments. The primary removal mechanism is production, deposition, and burial of organic matter in sediments. Although some phosphorus is lost from sediments during diagenesis, and some is converted from organic to inorganic phases through sink-switching (see Section 8.13.3.3.2), the phosphorus that remains within the sediment pile accumulating on the sea bottom is eventually recycled into the mantle, along with accompanying bioactive elements (e.g., carbon, nitrogen), upon subduction of the oceanic plate. Marine sedimentary organic matter undergoes metamorphism at the elevated temperatures and pressures experienced by the subducting plate, causing volatilization of organic carbon and nitrogen, with subsequent release as CO₂ and N₂. Because there is no quantitatively important phosphorus gas phase that forms under metamorphic conditions, sedimentary organic phosphorus on the subducting oceanic plate is likely incorporated into crystalline apatite during subduction-zone metamorphism. The net result is that subducted organic phosphorus cannot be returned to the Earth’s surface at the same rate as subducted organic carbon and nitrogen, and thus phosphorus is decoupled from carbon and nitrogen cycles during subduction and metamorphism. Furthermore, once exposed on land

through tectonic uplift processes, the phosphorus residing in crystalline rocks formed during subduction and metamorphism must be chemically weathered in order to supply bioavailable phosphorus to the ocean (Guidry *et al.*, 2000).

Thus, if phosphorus is the limiting nutrient for the ocean over geologic timescales, as has been the paradigm of geochemists (see Section 8.13.3.3.4 for summary of arguments for and against the paradigm of P-limitation), return of phosphorus to the Earth's surface via crystalline rock production, sediment uplift, and subsequent chemical weathering controls the amount of phosphorus returning to the ocean, and thus controls oceanic productivity over geologic timescales (Guidry *et al.*, 2000). In this way, Guidry *et al.* (2000) argue convincingly that tectonics may play the ultimate role in controlling the exogenic phosphorus mass, resulting in long-term P-limited productivity in the ocean.

8.13.3.4.2 *Links to other biogeochemical cycles on long, geologic timescales*

The nutrient–CO₂ connection. The biogeochemical cycles of phosphorus and carbon are linked through photosynthetic uptake and release during respiration (Section 8.13.3.3.2). During times of elevated marine biological productivity, enhanced uptake of surface water CO₂ by photosynthetic organisms results in increased CO₂ invasion from the atmosphere, which persists until the supply of the least abundant nutrient is exhausted. On geologic timescales, phosphorus is likely to function as the limiting nutrient and thus play a role in atmospheric CO₂ regulation by limiting CO₂ draw-down by oceanic photosynthetic activity. Because atmospheric CO₂ exerts a greenhouse warming effect, changes in phosphorus (or other nutrient) inventories can impact atmospheric CO₂ levels and play a role in global climate change. Several studies have argued that oceanic phosphorus has exerted just such an effect on climate, triggering or enhancing climate change on glacial–interglacial timescales (Broecker, 1982a,b; Boyle, 1990; Ganeshram *et al.*, 2002; Tamburini *et al.*, 2003).

In order to estimate paleoceanographic nutrient levels, and thereby explore links between nutrient variability, atmospheric CO₂ and climate change, a range of nutrient proxies have been developed. The ratio of cadmium (Cd) to calcium (Ca) in benthic foraminifera has been used as a proxy for dissolved phosphate, based on the observation that dissolved cadmium and phosphate concentrations are linearly correlated in modern oceanic waters (Boyle, 1988). While the basis of the Cd : PO₄ relationship is not understood, from either a biochemical or geochemical standpoint (e.g., Cullen *et al.*, 2003),

the Cd : Ca ratio in benthic foraminifera has found wide application as a proxy for dissolved phosphate in the paleo-ocean (see summary in Boyle, 1990). Important questions about the reliability of Cd : Ca as a phosphate proxy remain to be addressed. For example, since it appears that benthic phosphate flux from the seabed is a globally important source of phosphorus to the ocean (Colman and Holland, 2000), it is critical to examine the relative behavior of phosphate and cadmium during early diagenesis. Uncoupling of cadmium and phosphate during early diagenesis, with implications for uncoupled benthic flux of these elements, could negatively impact the reliability of the cadmium : phosphorus proxy (e.g., McCorkle and Klinkhammer, 1991; Rosenthal *et al.*, 1995a). It has been argued that the decoupling, although it has been documented, has minimal effects on the oceanic budgets of cadmium and phosphate (Rosenthal *et al.*, 1995b). Another consideration is, while cadmium may be a good proxy for phosphate, if dissolved organic phosphorus is important in phytoplankton nutrition, as seems likely (see Sections 8.13.3.3.3 and 8.13.3.3.4), the utility of the Cd : PO₄ proxy for assessing nutrient-constraints on levels of oceanic primary production may be diminished. This latter point suggests that it may be interesting to examine the relationship between cadmium and TDP, although it is still unclear what fraction of the DOP pool is bioavailable. Finally, it appears that phytoplankton Cd : PO₄ ratios vary as a function of environmental parameters that affect phytoplankton growth rates, suggesting that extrapolation from Cd : Ca ratios to surface phosphate concentrations may not be a straightforward endeavor (Cullen *et al.*, 2003).

The phosphorus–iron–oxygen connection. Phosphorus and oxygen cycles are linked through the redox chemistry of iron. Ferrous iron is unstable at the Earth's surface in the presence of oxygen, and oxidizes to form ferric iron oxyhydroxide precipitates, which are extremely efficient scavengers of dissolved phosphate (see Sections 8.13.3.1, 8.13.3.2 and 8.13.3.3.2). Resupply of phosphate to surface waters, where it can fertilize biological productivity, is reduced when oceanic bottom waters are well-oxygenated due to scavenging of phosphate by ferric oxyhydroxides. In contrast, during times in Earth's history when oxygen was not abundant in the atmosphere (Precambrian), and when expanses of the deep ocean were anoxic (e.g., Cretaceous), the potential for a larger oceanic dissolved phosphate inventory could have been realized due to the reduced importance of sequestering with ferric oxyhydroxides. This iron–phosphorus–oxygen coupling produces a negative feedback, which may have kept atmospheric O₂ within equitable levels throughout the Phanerozoic. The feedback

between atmospheric oxygen and phosphorus availability has been recognized in a number of studies (Kump, 1988; Berner and Canfield, 1989; Holland, 1990, 1994; Betts and Holland, 1991; Herbert and Sarmiento, 1991; Colman and Holland, 1994; Van Cappellen and Ingall, 1994a, b; Colman *et al.*, 1997; Petsch and Berner, 1998).

In some of the most recent work on this topic, Van Cappellen and Ingall formalize and explore this feedback through mass balance calculations using a coupled model of carbon, phosphorus, oxygen, and iron biogeochemical cycles, and conclude that oceanic P-cycling plays a determining role in long-term stabilization of atmospheric oxygen. Colman *et al.* (1997) take exception to some of the assumptions made in Van Cappellen and Ingall's work, and demonstrate that explicit inclusion of weathering rates, not included in the original model, markedly impacts the oceanic bioavailable P-inventory and affects the model's prediction of O₂ levels. Petsch and Berner (1998) incorporate the weathering rate effect demonstrated by Colman *et al.* (1997) into a revised coupled C–O₂–Fe–P model. Colman *et al.* (1997) also point out that questions remain concerning preferential P-regeneration from sedimentary organic matter under anoxic conditions, and this is a core condition of the negative feedback in Van Cappellen and Ingall's model. Further, according to subsequent work (Anderson *et al.*, 2001), it is unclear that sedimentary organic C : P ratios are a robust indicator of organic-P burial in any case, since diagenetic sink-switching entraps some portion of regenerated phosphorus from organic matter into secondary inorganic phases (see discussion in Section 8.13.3.3.2).

8.13.3.4.3 *Phosphorus in paleoceanography: P-burial as a Proxy for weathering, paleoproductivity, and climate change*

A number of studies have used records of phosphorus burial in marine sediments as direct indicators of weathering, delivery of bioavailable phosphorus to the oceans, paleoproductivity, and resultant impacts on climate through the nutrient–CO₂ connection (Filippelli and Delaney, 1994; Delaney and Filippelli, 1994; Filippelli, 1997a,b; Föllmi, 1995a,b). This is a challenging undertaking, as it is difficult to extrapolate from regional studies to global-scale phenomena, and many uncertainties remain about the geological, chemical, and biological controls on fluxes of phosphorus into and out of the ocean (Ruttenberg, 1994; this chapter). In a more regional study, Slomp *et al.* (2002) use P-speciation of sediments from Mediterranean cores to infer depositional conditions that existed during ancient sapropel

formation. In another type of paleoceanographic study, Tamburini *et al.* (2003) document sediment P-speciation in a North Atlantic sediment core in which they are able to correlate phosphorus geochemistry with Heinrich events (ice-rafting of terrestrially derived detrital material to the open ocean during glacial times). In this latter study, P-speciation is used to infer bottom water redox conditions and make inferences about water column stratification induced by enhanced freshwater input coincident with the Heinrich events. Variations in the global phosphorus cycle on a number of different timescales are reviewed by Compton *et al.* (2000), ranging from glacial–interglacial time periods to timescales greater than 1 Myr.

8.13.3.4.4 *Ancient phosphorites*

The episodic occurrence of phosphorite formation as implied from the episodic abundance of giant phosphorite deposits throughout the Phanerozoic rock record (Figure 16), has motivated questions about perturbations to the global phosphorus cycle throughout geologic time, and the implications of such perturbations on other global cycles of other bio-elements, and climate (Cook and McElhinney, 1979; Cook *et al.*, 1990; Arthur and Jenkyns, 1981; Föllmi, 1990; Donnelly *et al.*, 1990). The huge variations in P-removal implied by these enormous phosphorite deposits imply extreme perturbations to the global ocean. Among the paleoceanographic conditions that have been linked to the genesis of giant phosphorite deposits are ocean anoxic events (Cook and McElhinney, 1979; Arthur and Jenkyns, 1981), sea-level change (Arthur and Jenkyns, 1981; Sheldon, 1980; Riggs, 1984; Riggs *et al.*, 1985), and plate tectonics (Cook and McElhinney, 1979; Sheldon, 1980; Compton *et al.*, 2000). Several studies have suggested a link between phosphorite formation and evolution (Cook and Shergold, 1984; Donnelly *et al.*, 1990). These and other studies are reviewed by Cook *et al.* (1990). No master variable has been identified that can account for the formation of these giant phosphorite deposits, and it may be that the confluence of different factors were important at different times. There is still uncertainty about whether these giant phosphorite deposits represent increased input of reactive phosphorus to the ocean, or whether they instead represent regionally focused phosphorus removal resulting from changes in ocean circulation (e.g., large, sustained upwelling sites) and concentration by later reworking (Compton *et al.*, 2000). With the recent identification of disseminated CFA formation in nonphosphorite forming environments (see Section 8.13.3.3.2), it is interesting to speculate how superimposition of P-burial as disseminated CFA onto the occurrence

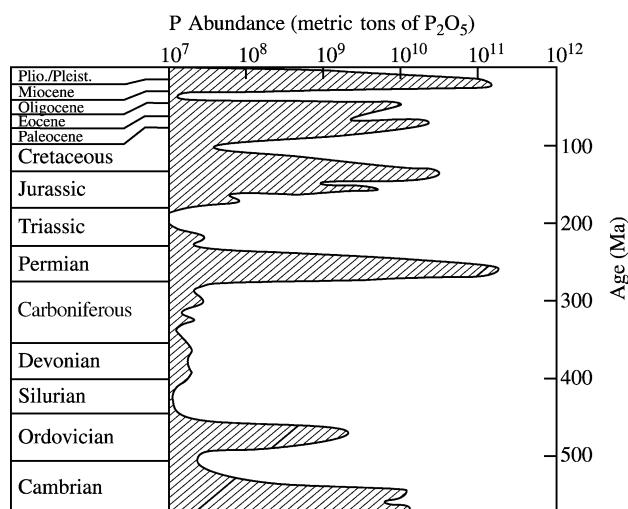


Figure 16 The abundance of phosphate in sedimentary rocks as a function of geologic age show episodicity of giant phosphorite deposition (after Cook and McElhinny, 1979).

of phosphorus in phosphorites throughout geologic time (Figure 16) would change perceptions of the global impact of phosphogenic events. Would the high P-abundances during periods of phosphorite formation be enhanced by addition of disseminated CFA burial in nonphosphorite environments, thus augmenting their suggestion of extreme conditions of oceanic P-removal? Or would disseminated CFA burial during nonphosphorite forming time periods minimize the valleys perceptible between eras of phosphorite giant deposition?

8.13.4 SUMMARY

The global cycle of phosphorus is truly a biogeochemical cycle, owing to the involvement of phosphorus in both biochemical and geochemical reactions and pathways. There have been marked advances since the 1990s on numerous fronts of phosphorus research, resulting from application of new methods, as well as rethinking of old assumptions and paradigms. An oceanic phosphorus residence time on the order of 10–20 kyr, a factor of 5–10 shorter than previously cited values, casts phosphorus in the role of a potential player in climate change on glacial–interglacial timescales through the nutrient–CO₂ connection. This possibility is bolstered by findings in a number of recent studies that phosphorus does function as the limiting nutrient in some modern oceanic settings. Both oxygen isotopes in phosphate ($\delta^{18}\text{O}-\text{PO}_4$) and *in situ* produced radiophosphorus isotopes (^{33}P and ^{32}P) are providing new insights into how phosphorus is cycled through metabolic pathways in the marine environment. ^{31}P -NMR and a new probe for

DOP-hydrolyzing enzymes are illuminating the composition of DOP and its importance for phytoplankton nutrition. Finally, new ideas about global phosphorus cycling on long, geologic timescales include a possible role for phosphorus in regulating atmospheric oxygen levels via the coupled iron–phosphorus–oxygen cycles, and the potential role of tectonics in setting the exogenic mass of phosphorus. The interplay of new findings in each of these areas, and others touched upon in this review chapter, are providing us with a fresh look at the global phosphorus cycle, one which is sure to evolve further as these and other new areas are explored in more depth by future studies.

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