

# VARIATIONS IN THE GLOBAL PHOSPHORUS CYCLE

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**ABSTRACT:** Phosphorus is a critical element in the biosphere, limiting biological productivity and thus modulating the global carbon cycle and climate. Fluxes of the global phosphorus cycle remain poorly constrained. The prehuman reactive phosphorus flux to the ocean is estimated to range from  $0.7\text{--}4.8 \times 10^{12}$  g/yr. Uncertainty in the reactive phosphorus flux hinges primarily on the uncertain fate of phosphate adsorbed to iron oxyhydroxide particles which are estimated to constitute 50% or more of the chemically weathered-phosphorus river flux.

Most reactive phosphorus is initially removed from seawater by burial of organic matter and by scavenging onto iron–manganese oxide particles derived from mid-ocean ridge (MOR) hydrothermal activity. Calculation of the oceanic phosphorus burial flux is complicated by early diagenetic redistribution of both oceanic and terrestrial phosphorus. Increased phosphorus input during periods of warm, humid climate is offset to some degree by increased burial rate as productivity shifts to expanded shallow-water estuary and shelf areas where phosphorus is rapidly decoupled from organic matter to form phosphorite. Phosphorus scavenging is greater if high sea levels are associated with increased MOR hydrothermal activity such as during the Late Cretaceous. Less phosphorus is derived from weathering during cool, dry climatic periods but a more direct transportation of phosphorus to the deep ocean, and a shift of productive upwelling regions to deeper water areas allows more phosphorus to be recycled in the water column. Lowered sea level results in less effective trapping of phosphorus in constricted estuary and shelf areas and in an increase in the phosphorus flux to the deep ocean from sediment resuspension. A decrease in MOR spreading rates and the resulting decrease in phosphorus scavenging by iron–manganese oxide particles would result in more phosphorus for the biosphere. Orogeny and glaciation may accelerate chemical weathering of phosphorus from the continents when the increased particle flux is exposed to warm and humid climate. Large, reworked phosphorite deposits may proxy for short-term organic carbon burial and correspond to periods of increased reactive phosphorus input that cannot be accommodated by long-term organic matter and iron-oxide particulate burial.

## INTRODUCTION

The weathering of phosphorus and its delivery and fate in the ocean are important aspects of the phosphorus cycle to understand because phosphorus is a limiting nutrient to biological productivity on geologic time scales. Much of the phosphorus delivered to the ocean has the potential to participate in biological production, but whether it does or bypasses the ocean reservoir is poorly understood. Reactive phosphorus, defined here as phosphorus that enters the ocean reservoir and is available for biological uptake, is of particular interest because it links the phosphorus and carbon cycles. Variations in the reactive phosphorus entering the oceans related to changes in climate and tectonism would impact the uptake of  $\text{CO}_2$  by primary productivity in the oceans, and the transfer of carbon as organic matter to the deep ocean to be oxidized or buried in sediments. The phosphorus cycle is simplified somewhat by the fact that there are no appreciable gaseous atmospheric phosphorus compounds, but the path of phosphorus from its release by chemical weathering to its transport and burial at sea is complex because of the inter-

action of phosphorus with the biosphere and iron–manganese oxide particles. A key question of interest to geochemists is how has the amount of reactive phosphorus entering the oceans varied in the past and can these variations be inferred from the geological record of reactive phosphorus sinks?

There have been a number of previous global phosphorus budgets proposed (Froelich et al., 1982; Richey, 1983; Froelich, 1984; Ruttenger, 1993; Filippelli and Delaney, 1994; Baturin et al., 1995) as well as reviews of our current understanding of the phosphorus cycle (Bentor, 1980; Arthur and Jenkyns, 1981; Glenn et al., 1994b; Föllmi, 1996). This paper presents a brief overview of our quantitative understanding of the reservoirs and fluxes of the global phosphorus cycle with an emphasis on recent results and remaining key uncertainties. The rapid exchange of phosphorus among different reservoirs combined with large anthropogenic influences make it difficult to quantify the amount of phosphorus entering the oceans. Measuring the output of reactive phosphorus from the oceans is hampered by the large area of the seafloor and the redistribution of phosphorus during early burial diagenesis. Processes operating on glacial/interglacial and longer (>1 m.y.) geologic time scales are discussed that might result in variations in the global phosphorus cycle with a particu-

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lar focus on the relationship of phosphorite deposits to changes in the amount of phosphorus entering the ocean.

#### THE GLOBAL PHOSPHORUS CYCLE

##### *Weathering Sources of Phosphorus to the Ocean*

The objective is to quantify the principal sources and sinks of marine phosphorus, and to differentiate between prehuman and present-day (polluted) phosphorus fluxes, as well as reactive and nonreactive phosphorus fluxes (Tables 1A, B). A simplified schematic of the global phosphorus cycle indicates that the river flux dominates phosphorus input to the ocean (Fig. 1). The other significant source is eolian particulate phosphorus. River input can be divided into dissolved inorganic phosphorus (DIP), dissolved organic phosphorus (DOP), particulate inorganic phosphorus (PIP), and particulate organic phosphorus (POP).

##### *Dissolved inorganic phosphorus.—*

The dissolved inorganic phosphorus (DIP) flux of rivers (orthophosphate,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) is estimated to be  $0.26$  to  $0.46 \times 10^{12}$  g/yr using a value of  $7$ – $10$   $\mu\text{g/l}$  as the average phosphorus concentration in unpolluted rivers (Meybeck, 1982; 1993; Savenko and Zakharova, 1995) and a river water flux of between  $3.7$  to  $4.6 \times 10^{16}$  kg/yr (Baumgartner and Reichel, 1975; Holland, 1978). The DIP value of  $7$ – $10$   $\mu\text{g/l}$  is derived from analyses of the least polluted rivers. The DIP in most rivers is influenced by human activities with DIP concentrations in agricultural and industrial areas as high as  $100$  to  $700$   $\mu\text{g/l}$  (Meybeck, 1993; Savenko and Zakharova, 1995). Pollution is estimated to increase the present-day DIP river flux to between  $0.8$  and  $1.4 \times 10^{12}$  g/yr (Meybeck, 1982).

##### *Dissolved organic phosphorus.—*

The present-day dissolved organic phosphorus (DOP) river flux can be calculated as  $0.55$  to  $0.68 \times 10^{12}$  g/yr from an aver-

age DOP concentration of  $15 \mu\text{g/l}$  in rivers (total dissolved phosphorus (TDP) of  $25 \mu\text{g/l}$  minus dissolved inorganic phosphorus of  $10 \mu\text{g/l}$ ) (Meybeck, 1982). Alternatively, the DOP flux can be calculated as  $0.2 \times 10^{12}$  g/yr from a dissolved organic carbon flux of  $0.22 \times 10^{15}$  g/yr and an average DOC C/P weight ratio of  $1000$  (Meybeck, 1982). The lower value ( $0.2 \times 10^{12}$  g/yr) is preferred because high TDP values can be obtained from unfiltered or polluted water samples (Meybeck, 1982).

##### *Particulate organic phosphorus.—*

Particulate organic phosphorus (POP) was originally calculated by Meybeck (1982) to be  $8 \times 10^{12}$  g/yr using a particulate organic matter (POM) C/P wt ratio of  $22$ , but Ramirez and Rose (1992) determined a much higher POM C/P wt ratio of  $193$ . Using a POM C/P ratio of  $193$  and  $0.17 \times 10^{15}$  g/yr for the terrestrial POM flux (Meybeck, 1993) gives a POP flux of  $0.9 \times 10^{12}$  g/yr (Ramirez and Rose, 1992). The POP is associated with the POM flux from soils ( $94 \times 10^{12}$  g/yr) and shales ( $76 \times 10^{12}$  g/yr) (Meybeck, 1993). Assuming a POM C/P wt ratio of  $193$ , gives a POP flux of  $0.5 \times 10^{12}$  g/yr from soils and  $0.4 \times 10^{12}$  g/yr from shales.

##### *Particulate inorganic phosphorus.—*

The particulate inorganic phosphorus (PIP) flux includes detrital phosphorus and adsorbed phosphorus. Detrital phosphorus refers to phosphorus that occurs in detrital grains, primarily igneous, metamorphic and sedimentary apatites as well as a trace element in other minerals. Detrital phosphorus is generally covalently bonded in mineral structures and not available for uptake by the biosphere or by adsorption until released by chemical weathering. Adsorbed phosphorus occurs primarily on iron-manganese oxide and oxyhydroxide particle surfaces (Palmer, 1985). Adsorbed phosphorus is potentially available to the biosphere through reversible exchange and is referred to here as iron-bound PIP. The detrital phosphorus and iron-bound PIP fluxes, Table 1A, were estimated from the total and chemically weathered river fluxes of phosphorus. The chemically

TABLE 1A.—SUMMARY OF PREHUMAN PHOSPHORUS FLUX TO THE OCEAN ( $\times 10^{12}$  g/yr)

Riverine Phosphorus	
DIP	0.3–0.5
DOP	0.2 (maximum)
POP (0.5 soil derived; 0.4 shale derived)	0.9 (maximum)
PIP, Fe-bound (P adsorbed to iron-manganese oxide/oxyhydroxides)	1.5–3.0
PIP, detrital	6.9–12.2
Total river phosphorus	9.8–16.8
Eolian phosphorus	1.0 (20% reactive)
Total River + Eolian phosphorus flux	10.8–17.8
Total prehuman potentially reactive phosphorus flux	3.1–4.8
(DIP+DOP+POP+iron-bound PIP+reactive Eolian)	

TABLE 1B.—SUMMARY OF PRESENT-DAY PHOSPHORUS FLUX TO THE OCEAN ( $\times 10^{12}$  g/yr)

DIP	$0.8$ – $1.4 \times 10^{12}$ g/yr
DOP	0.2 (average)
POP (0.5 soil derived; 0.4 shale derived)	0.9 (average)
PIP, Fe-bound (P adsorbed to iron-manganese oxide/oxyhydroxides)	1.3–7.4
PIP, detrital	14.5–20.5
Total river phosphorus	17.7–30.4
Eolian phosphorus	1.05 (20% reactive)
Total River + Eolian phosphorus flux	18.7–31.4
Total present-day potentially reactive phosphorus flux	3.4–10.1
(DIP+DOP+POP+iron-bound PIP+20% Eolian)	

**GLOBAL PREHUMAN PHOSPHORUS<sup>1</sup> CYCLE**

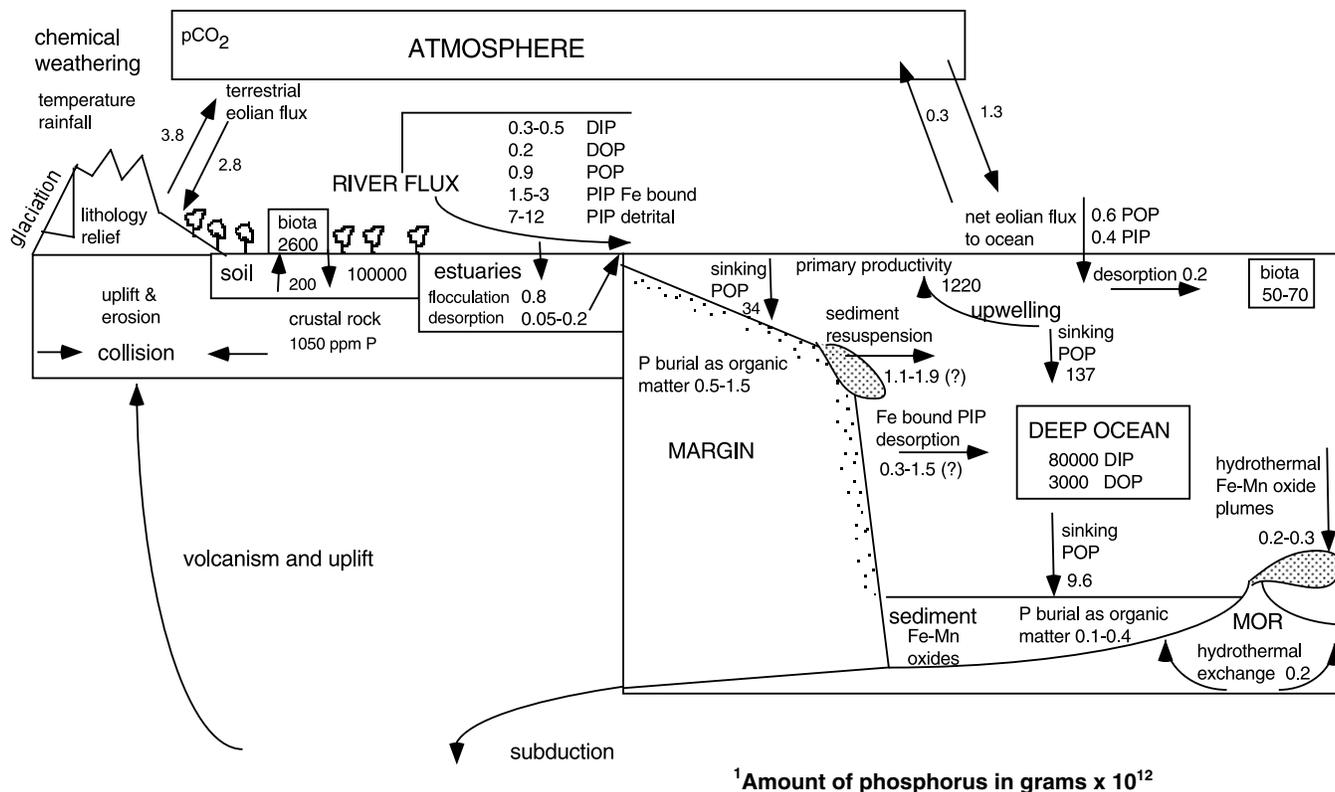


FIG. 1.— The global, prehuman phosphorus cycle with an outline of the major fluxes in units of 10<sup>12</sup>g/yr (arrows indicate direction of flux) and amount of phosphorus in reservoirs in units of grams x 10<sup>12</sup>. Sources of data and flux calculations are discussed in the text. Also included are factors important to the total potentially reactive phosphorus flux to the ocean, such as uplift and erosion. Net primary productivity and sinking particulate values assume a Redfield C/P wt ratio of 41 and that approximately 80% of primary production is over the open ocean and approximately 14% of primary production sinks below the photic zone (Martin et al., 1987). The net eolian flux from the continents to the ocean is 1x10<sup>12</sup>g/yr, of which 20% is estimated to desorb in surface waters (Graham and Duce, 1979). The flux derived from desorption of iron-bound PIP (0.05–0.2 x 10<sup>12</sup>g) is considered to be a subset of the sediment resuspension flux (1.1–1.9 x 10<sup>12</sup>g); both fluxes are poorly constrained. DIP = dissolved inorganic phosphorus; DOP = dissolved organic phosphorus; PIP = particulate inorganic phosphorus; POP = dissolved organic phosphorus.

weathered phosphorus flux includes DIP, DOP, POP (soil derived), and iron-bound PIP. The total prehuman phosphorus river flux was calculated to be 9.8–16.8 x 10<sup>12</sup>g/yr (Table 1A) by assuming that the total present-day sediment load of 1.4–2.4 x 10<sup>16</sup>g/yr (Milliman and Zvyvitski, 1992) is twice that of the prehuman sediment load (Bernier and Bernier, 1987), that 21–26% of total prehuman weathering is chemical (see arguments below), that crustal rocks have an average phosphorus content of 1050 ppm (Mason, 1967), and that phosphorus is not preferentially leached from crustal rocks. The chemically weathered prehuman phosphorus flux is 2.5–4.2 x 10<sup>12</sup>g/yr. The PIP flux assumed to occur primarily as exchangeable iron-bound phosphorus is 1.5–3 x 10<sup>12</sup>g/yr and was calculated as the difference between the total chemically weathered flux and the sum of DIP, DOP and POP fluxes (Table 1A). A similar iron-bound phosphorus input by fluvial particulates of 0.4–4 x 10<sup>12</sup>g/yr was estimated by Froelich (1988). The river phosphorus flux is dominated by the detrital phosphorus flux (6.9–12.2 x 10<sup>12</sup>g/yr) which was calculated as the difference between the total river phosphorus flux and the chemically weathered plus shale-derived POP fluxes.

*Eolian flux.—*

The eolian phosphorus flux to the ocean was estimated to be 1 x 10<sup>12</sup>g/yr, mostly particulate phosphorus, by Graham and Duce (1979). The eolian flux of terrestrial POM carbon was estimated to be 0.1 x 10<sup>15</sup> g/yr (Romankevich, 1984; Zafiriou et al., 1985). Assuming that most of the POM is soil derived with a C/P wt ratio of 154 (Ramirez and Rose, 1992) gives an eolian POP flux of 0.6 x 10<sup>12</sup>g/yr. Therefore, the eolian flux is roughly equally split between PIP and POP. Approximately 20% of the total eolian phosphorus flux is readily soluble in seawater and is an important source of phosphorus for non-upwelling ocean areas (Graham and Duce, 1982). Human activities have increased the eolian dust flux of phosphorus to the ocean by only 0.05 x 10<sup>12</sup>g/yr (Graham and Duce, 1979).

*Prehuman phosphorus input.—*

The total (riverine plus eolian) prehuman phosphorus flux to the oceans ranges from 10.8–17.8 x 10<sup>12</sup>g/yr (Table 1A). The total potentially reactive phosphorus flux, defined as the sum of the chemically weathered flux, shale-derived POP flux, and 20% of the eolian flux, is estimated to be 3.1–4.8 x 10<sup>12</sup>g/yr.

The ranges in detrital and iron-bound PIP fluxes reflect the range estimated for the prehuman total sediment load of rivers ( $0.7\text{--}1.2 \times 10^{16}\text{g/yr}$ ) and also depends on the extent of chemical weathering (17–26%), whereas the range in DIP reflects the range in total river water flux ( $3.7\text{--}4.6 \times 10^{16}\text{kg/yr}$ ). Present-day POP and DOP fluxes of  $0.9$  and  $0.2 \times 10^{12}\text{g/yr}$ , respectively, are assumed to be maximum values because the anthropogenic influence is difficult to quantify (Meybeck, 1993). It appears that no more than 20% of the total river flux of POM and DOM is preserved in sediments (Hedges, 1992), which would correspond to around  $0.9 \times 10^{12}\text{g/yr}$  reactive organic phosphorus, but where and on what time scale this terrestrial organic flux is remineralized remain unclear. The largest pool of potentially reactive phosphorus is iron-bound PIP. Based on the range in potentially reactive phosphorus input and a deep ocean phosphorus reservoir of approximately  $8 \times 10^{16}\text{g}$ , a residence time of phosphorus in the ocean of 16–27 kyr can be predicted, but a phosphorus residence time on the order of 100 kyr would be predicted if much of the particulate phosphorus flux (POP and iron-bound PIP) is nonreactive during its transit through the ocean. A critical question that remains is: What fraction of the terrestrial iron-bound PIP is released to the oceans?

#### *Present-day phosphorus input.—*

For comparison, the total present-day phosphorus river flux (Table 1B) was calculated to be  $17.7\text{--}30.4 \times 10^{12}\text{g/yr}$  from a total sediment load of  $1.4\text{--}2.4 \times 10^{16}\text{g/yr}$  (Milliman and Zuyvitski, 1992) and assuming that 17% of present-day total weathering is chemical (Garrels and Mackenzie, 1971). The chemically-weathered phosphorus flux is  $3\text{--}5.2 \times 10^{12}\text{g/yr}$ . If only 10% of present-day total weathering is chemical (Berner and Berner, 1996), then the chemically-weathered phosphorus flux would be  $1.8\text{--}3.0 \times 10^{12}\text{g/yr}$ .

It is difficult to calculate the present-day iron-bound PIP flux, because of the higher DIP flux associated with pollution, and because much of the present-day sediment load of rivers is from accelerated soil erosion (Berner and Berner, 1987). The amount and mineralogy of the iron oxides transported by rivers and their relative stability in estuarine and marine environments remain poorly understood. For example, ferrihydrite is common in young soils as a precursor to hematite and its high surface area should make it a labile source of adsorbed phosphorus. A rough estimate of the iron-bound PIP river flux is calculated to be  $1.3\text{--}7.4 \times 10^{12}\text{g/yr}$  (Table 1B) assuming a 2 wt% average iron oxide content of the river sediment load, an iron oxide surface area of  $60\text{--}200\text{ m}^2/\text{g}$ , and a maximum phosphate adsorption by iron oxide of  $2.5\text{ }\mu\text{mol}/\text{m}^2$  (Schwertmann and Taylor, 1989). The calculated iron-bound PIP flux is 8–26% of the total PIP flux, which is similar to the estimated 15–30% iron-bound PIP flux of the St. Lawrence River (Lucotte and d'Anglejan, 1983). The present-day minimum potentially reactive phosphorus flux ( $3.4 \times 10^{12}\text{g/yr}$ ) is similar to that of the prehuman flux, but the maximum present-day potentially reactive flux is roughly twice that of the prehuman value (Table 1B).

#### *Chemical weathering.—*

The extent of chemical weathering is critical because it determines the flux of potentially reactive phosphorus to the oceans. The percent of total weathering (chemical and mechanical) that is chemical is calculated by dividing the mass of the dissolved load by the mass of the dissolved load plus sediment load carried by rivers. The mass of the dissolved load was calculated from average global river concentrations corrected for human influences and for bicarbonate ion derived from atmospheric and soil  $\text{CO}_2$  (Table 2).

The present-day total dissolved load from chemical weathering is  $0.32\text{--}0.41 \times 10^{16}\text{g/yr}$  or 15–19% of the total weathering flux. This range includes the global average of 17% estimated by Garrels and Mackenzie (1971), but is higher than the estimate of 10% by Berner and Berner (1996). Chemical weathering would make up 21–26% of the total weathering flux using a prehuman dissolved load (Table 2) and assuming a doubling of the prehuman sediment load (Berner and Berner, 1987).

The relative amount of reactive phosphorus in rivers derived from chemical weathering of apatite as opposed to other phosphorus-bearing minerals is unknown, but detrital igneous and metamorphic apatites are probably no more susceptible to dissolution than many other minerals containing minor to trace amounts of phosphorus (Zanin, 1989). The average total particulate phosphorus (TPP=PIP+POP) content of present-day rivers is estimated to be  $1150\text{ }\mu\text{g/g}$  (Martin and Meybeck, 1979; Meybeck, 1982). Subtraction of soil-derived POP and iron-bound PIP (Table 1B) from TPP indicates that the phosphorus content of the detrital weathering flux (POP from shales and detrital PIP) is comparable to the average phosphorus content of crustal rocks and suggests that phosphorus is not preferentially removed (leached) from fresh rock during chemical weathering.

TABLE 2.— AVERAGE RIVER WATER CONCENTRATIONS (mg/kg)

	Present day Livingstone (1963)	Prehuman (total) Meybeck (1979)	Prehuman Rock-derived
Na	6.3	5.1	5.1
Mg	4.1	3.3	3.3
Ca	15	13.4	13.4
K	2.3	1.3	1.3
SiO <sub>2</sub>	13.1	10.4	10.4
Cl	7.8	5.7	5.7
SO <sub>4</sub>	11.2	8.2	8.2
HCO <sub>3</sub>	58.4	52	21.5*
Fe	0.67		
F	1		
Total	120	99.4	68.9

\*The dissolved mass is corrected for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  uptake from the atmosphere by assuming one-third of the dissolved inorganic carbon, mostly present as bicarbonate ion, is from the weathering of carbonate rocks and one-third is from weathering of silicate rocks by carbonic acid (Meybeck, 1993).

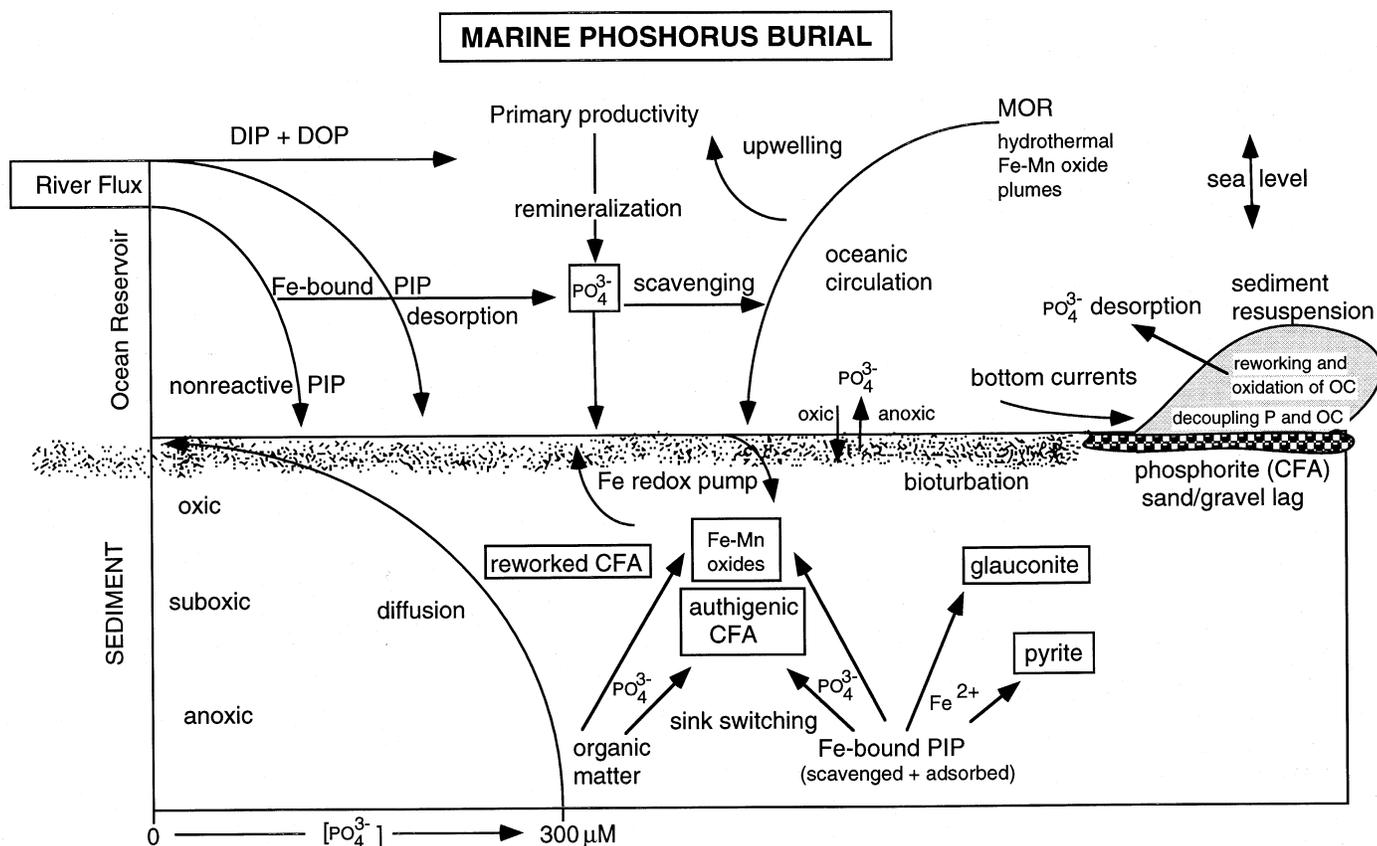


FIG. 2.— Overall schematic of the processes involved in the burial of phosphorus in marine sediments. After burial, most of the organic matter and iron-manganese oxyhydroxide primary phosphorus is released and taken up by authigenic CFA and iron-manganese oxide surfaces in the sediment during diagenesis. This redistribution (sink switching) makes it difficult to determine the net reactive phosphorus burial flux in marine sediments, particularly on continental margins having abundant iron-bound PIP, and possibly reworked CFA.

#### *Reflux of Phosphorus from Sediments to Seawater*

Phosphorus buried in sediments can later be remobilized during bacterial degradation of organic matter and reduction of iron oxides, with phosphate ion concentrations commonly increasing up to several hundred micromolar within meters of the sediment/seawater interface (Fig. 2). Most of this remobilized phosphate is removed from the pore water as authigenic carbonate fluorapatite (CFA) or is sorbed by iron oxide particles and does not return to the ocean reservoir (Krom and Berner, 1981; Ruttenger and Berner, 1993; Ingall and Jahnke, 1994; Lucotte et al., 1994; Filippelli and Delaney, 1996). However, when sediment is resuspended in estuaries and on the shelf, significant amounts of DIP may be released into the water column by desorption (Fox et al., 1986; Sundby et al., 1992). Resuspension of sediment is predicted to result in desorption of PIP because the phosphate ion concentrations in pore waters are much higher than in bottom waters. Berner and Rao (1994) estimate that 5  $\mu g$  of phosphorus per kg of resuspended sediment is released on the Amazon shelf, which translates to a potentially large global resuspension phosphorus flux of  $1.1\text{--}1.9 \times 10^{12}$  g/yr. Clearly more data are needed to quantify phosphorus flux by sediment resuspension. Significantly more phosphorus may diffuse from near surface sediments back into the ocean reservoir where low oxygen concentration in the bottom waters render

iron oxide trapping of phosphorus less efficient (Ingall et al., 1993; Ingall and Jahnke, 1994; Van Cappellan and Ingall, 1994). Although present-day anoxic bottom waters are minor, more widespread ocean anoxia may have occurred during certain periods of Earth history.

#### *Role of Estuaries*

The highly variable biological and physical dynamics of estuaries make it difficult to estimate the net phosphorus river flux to the ocean (Wollast, 1983; Froelich, 1984). The conservative mixing behavior of DOC in estuaries would suggest that most DOC and associated DOP is delivered to the sea and perhaps 5–10% is trapped in estuaries by flocculation of primarily humic compounds (Sholkovitz, 1976; Sholkovitz et al., 1978; Burton, 1983). However, most DOC in the ocean appears to be derived from marine rather than riverine sources and suggests that most riverine DOC is photohydrolyzed to smaller compounds and recycled by bacteria within estuaries and coastal systems (see review by Hedges, 1992). Apparently most riverborne particulate organic matter (POM) and associated POP is removed in estuarine sediments before reaching coastal or shelf areas (Wollast, 1983). However, carbon isotope, C/N ratio, and biomarker data indicate that a significant fraction of the organic

matter buried on margins adjacent to large rivers (Prahl et al., 1994) as well as in deep-sea sediments (Druffel et al., 1986) can be terrestrial.

The river water DIP flux appears to be enhanced by desorption of iron-bound PIP in estuaries. Chase and Sayles (1980) observed as much as 3% phosphate desorption associated with an increase in pH during mixing. Froelich (1984) found that the DIP river flux may increase by 50% during passage through estuaries. Extrapolation of these results suggests a global desorption flux to estuaries of  $0.05\text{--}0.23 \times 10^{12}\text{g/yr}$ . A phosphorus mass balance of the Scheldt estuary indicates that much of the phosphate entering the estuary is deposited rather than being directly transported to sea (Wollast, 1983). Considering the above estimates, estuaries may trap approximately one-quarter of the total potentially reactive phosphorus river flux as DOP and POP, as well as a significant but unknown amount of the iron-bound PIP flux. Efficient phosphorus trapping by estuaries is supported by Holocene reactive phosphorus accumulation rates of  $1,000\text{--}11,000 \mu\text{mol/cm}^2/\text{kyr}$ , which are an order of magnitude greater than the typical phosphorus accumulation rates on continental margins (Filippelli, 1997a; unpublished data).

#### Oceanic Sinks of Phosphorus

The combined primary sedimentary sinks of reactive phosphorus in the ocean are estimated to range from  $1\text{--}2.5 \times 10^{12}\text{g/yr}$  (Table 3A). Uptake of phosphorus by organisms is the dominant primary sink of reactive phosphorus in the ocean (Table 3A). The burial rate of phosphorus associated with organic matter is estimated to be  $0.6\text{--}1.9 \times 10^{12}\text{g/yr}$  assuming an organic carbon burial flux of  $10\text{--}30 \times 10^{12} \text{mol/yr}$  (Mackenzie et al., 1993) having an average sedimentary C/P molar ratio of 500 (Ramirez and Rose, 1992). In addition to long-term organic carbon burial, short-term ( $<10^5$  yr) variations in organic carbon burial includes organic matter regenerated on or just below the seafloor (Jørgensen, 1983) where released phosphorus can be captured as CFA or adsorbed onto oxyhydroxides, thereby decoupling phosphorus from the nutrient flux back to the ocean. Short-term organic carbon burial is expected to increase the significance of the organic matter primary sink of phosphorus, particularly in shallow-water shelf regions. The range in phosphorus burial estimated by Ruttenberg (1993) and Berner and Berner (1996) (Table 3B) overlaps with estimates of the total potentially reactive phosphorus input (Table 1A), but is near the upper limit of the estimated primary phosphorus burial sinks (Table 3A). The high phosphorus burial estimates of Filippelli and Delaney (1996) (Table 3B) may include a significant amount of nonreac-

TABLE 3A.—OCEANIC SINKS OF REACTIVE PHOSPHORUS ( $\times 10^{12}\text{g/yr}$ )

Organic matter	0.6–1.9
iron oxides (MOR)	0.4–0.5
CFA (direct precipitation)	0–0.1 (?)
TOTAL	1.0–2.5

tive phosphorus or detrital/reworked CFA especially on continental margins.

Nonbiological phosphorus sinks in the ocean are important because they influence the deep water phosphate ion concentration and amount of upwelled phosphorus available for primary productivity. Wheat et al. (1996) estimate that the total amount of phosphorus removed by hydrothermal processes associated with mid-ocean ridges (MOR) is between  $0.37\text{--}0.5 \times 10^{12}\text{g/yr}$ , most of which ( $0.17\text{--}0.31 \times 10^{12}\text{g/yr}$ ) is DIP removed by iron oxides entrained in nonbuoyant plumes. An additional  $0.2 \times 10^{12}\text{g/yr}$  is removed during the convective flow of seawater through ridge flanks. Although 30–100% of the phosphate is removed from seawater circulating through basalt, the total amount of phosphorus removed by this process is minor ( $0.004 \times 10^{12}\text{g/yr}$ ). The amount of phosphorus uptake by particulate iron oxides in hydrothermal plumes depends on the intensity of hydrothermal activity and the phosphate concentration of the ambient seawater (Feely et al., 1990; 1991). The net amount of phosphorus scavenged from the oceanic water column by iron-manganese oxide-coated eolian or detrital particles is probably less than that removed by fresh MOR iron precipitates, because some phosphorus is adsorbed before entering the ocean. In addition, eolian iron-manganese dust partially desorbs phosphorus in surface waters and may enhance primary production (Graham and Duce, 1982).

CFA precipitated directly on the seafloor is generally not believed to be a significant phosphorus sink. Phosphatic hardgrounds apparently form slowly during extended periods of non-deposition (persistent bottom currents), and because hardgrounds commonly form at the upper surface of carbonate

TABLE 3B.—COMPARISON OF DIFFERENT PHOSPHORUS BURIAL BUDGETS ( $\times 10^{12}\text{g/yr}$ )

Sink	Ruttenberg (1993)*	Berner and Berner (1996)
Org Matter (O-P)	1.3	1.1
iron-oxides (iron-P)	1.2 (0.1)	0.7
CFA	2.8 (0.7)	1.1
loosely-sorbed P	0.4	—
TOTAL	5.7 (2.4)	2.9

\*Calculated from sequential extraction data of marine sediments and the flux of riverine suspended material to the margins and deep sea (minimum values in parentheses). CFA includes fish debris and carbonate-bound phosphorus.

Sink Area	Filippelli and Delaney (1996)
Low Productivity	0.2
Moderate to high Productivity	2.4
Continental Margins	3.9
TOTAL	$6.5 \times 10^{12}\text{g/yr}$

Calculated as the mean phosphorus accumulation rate over last one million year multiplied by area.

substrate rocks, they are not volumetrically significant (e.g., Föllmi and Garrison, 1991). Another possible mechanism of phosphorus uptake in sediments is by iron redox pumping (Heggie et al., 1990; O'Brien et al., 1990). The iron redox phosphorus pump works by adsorption of phosphate ion from bottom and interstitial waters onto iron oxides, release of this phosphate for CFA formation upon reduction of the iron oxides at depth in the sediment, and then oxidation of the iron as it diffuses across the redox boundary. The amount of reactive phosphorus taken up directly from bottom waters by the iron redox pump mechanism is probably relatively small because most of the iron reduction and oxidation cycle occurs at depth in the sediment where it is overlain by oxygenated bottom waters.

#### *Diagenetic Redistribution of Buried Phosphorus*

A major cause of uncertainty in estimates of the reactive phosphorus burial flux in marine sediments is the difficulty in distinguishing between phosphorus removed from the ocean reservoir (a true sink) as opposed to phosphorus that bypasses the ocean reservoir but is released into pore waters and taken up by CFA or iron-oxides during diagenesis (Fig. 2). Sequential extraction techniques have provided accumulation rate data on the various reservoirs of sedimentary phosphorus and have demonstrated the complex dynamics of phosphorus during burial diagenesis (Ruttenberg, 1993; Filippelli and Delaney, 1996). Diagenetic redistribution of phosphorus (sink switching) involves much of the phosphorus that arrives at the seafloor and can complicate the determination of the primary reactive phosphorus output. CFA is not a true sink of reactive phosphorus if it is reworked CFA or phosphorus derived from iron-bound PIP that bypassed the ocean reservoir. The detrital phosphorus flux will include some fraction of reworked sedimentary CFA either locally derived or carried by rivers. The detrital CFA content of river sediment loads is unknown, but is expected to be significant particularly during marine regressions when rivers erode older deposits containing authigenic CFA.

CFA is estimated to make up 30–50% of the total reactive phosphorus output (Ruttenberg, 1993; Table 3B). Fine-grained, disseminated, and hence not easily detected, CFA containing phosphorus derived from both iron-bound PIP and organic phosphorus may occur in detrital-rich continental margin sediments (Ruttenberg and Berner, 1993) and in deep sea sediments (Filippelli and Delaney, 1996). Berner and Berner (1996) using the data of Ruttenberg and Berner (1993) estimate the phosphorus sink associated with finely dispersed authigenic CFA to be  $1 \times 10^{12}$  g/yr, which is comparable to the organic matter phosphorus burial sink. But what percentage of the phosphorus in authigenic CFA is derived from organic matter vs. iron-bound PIP?

The phosphorus in most large phosphorite deposits is derived from the microbial release of organic phosphorus, as indicated by the common association of phosphorite deposits and reworked and condensed sediments below strong upwelling systems (Bentor, 1980). CFA containing phosphorus derived from iron-bound PIP is limited by the amount of iron-rich ter-

igenous sediment. The lateral or overlapping association of phosphorite deposits with iron-rich authigenic minerals (glauconite, pyrite, and ferruginous crusts) as observed on the Peru-Chile continental margin (Glenn et al., 1994a,b) and southwest African continental margin (Birch et al., 1983; Birch, 1990) suggests that some CFA phosphorus is derived from a large pool of iron-bound PIP. For example, Late Cretaceous Egyptian phosphorite deposits may have formed largely from remobilized iron-bound PIP derived from local rivers (Glenn and Arthur, 1990; Glenn et al., 1994a). The near-absence of glauconite in Neogene phosphorites on the Florida Platform (Riggs, 1984), in contrast to the large glauconite content of Neogene sediments on the New Jersey margin, suggests an increasingly abundant source of iron-bound phosphate associated with terrigenous sediment input to the continental margin. High pore water phosphate concentrations and the presence of authigenic CFA in places (Mountain et al., 1994) suggest that significant amounts of iron-bound PIP are released to form CFA in rapidly deposited, terrigenous sediment on the New Jersey margin.

The large amount of phosphorus (Froelich, 1984) associated with iron-manganese oxide crusts on biogenic carbonate is probably derived mostly from organic and iron-bound phosphorus in the sediment rather than phosphorus taken up directly from the water column (Palmer, 1985). Precipitation of REE phosphate minerals in marine sandstones has been proposed as a major sink of oceanic phosphorus, on the order of  $2.3 \times 10^{12}$  g/yr (Rasmussen, 1996; also see Rasmussen, this volume), but REE phosphate minerals probably form during sediment diagenesis with phosphorus derived from both reactive and nonreactive phosphorus sources.

#### DISCUSSION

Most of the phosphorus delivered to the ocean bypasses the marine biosphere. The prehuman reactive phosphorus flux to the oceans could be as small as  $0.7 \times 10^{12}$  g/yr and as much as  $4.8 \times 10^{12}$  g/yr (7–25% of the total phosphorus river flux). The bulk of the phosphorus that bypasses the ocean reservoir is detrital phosphorus ( $6.9$ – $12.2 \times 10^{12}$  g/yr). In addition, roughly half of the prehuman chemically weathered phosphorus flux of  $2.5$ – $4.2 \times 10^{12}$  g/yr is apparently adsorbed to iron oxides or is in particulate organic matter and bypasses the ocean reservoir. Assuming the entire dissolved phosphorus flux (DIP+DOP) and 20% of the eolian flux is reactive, the estimated reactive phosphorus burial flux would require that approximately 12–40% of the total potentially reactive particulate phosphorus flux (POP and iron-bound PIP) be released to the oceans as reactive phosphorus. These values are consistent with previous estimates of the soluble-exchangeable fraction of the total river particulate phosphorus of 3–6% (Chase and Sayles, 1980; Hedley et al., 1982; Van Eck, 1982; Tiessen et al., 1984).

What processes might change the reactive phosphorus flux to the ocean? A key assumption is that the reactive phosphorus river flux varies directly with chemical weathering rates. However, the rapid and reversible reactions of DIP, such as adsorption-desorption from iron oxyhydroxide surfaces, uptake

by primary producers in river water, and burial in sediments, may buffer changes in the DIP concentration (Wollast, 1983; Froelich, 1988). Although buffering of DIP concentrations is not supported by the high DIP concentration in present-day polluted rivers, these extreme levels of phosphorus entering rivers today may have exceeded the natural buffering capacity of rivers. Natural increases in DIP would be much less than for polluted rivers and may have been moderated by increased uptake as organic phosphorus (DOP and POP) or as iron-bound PIP. The chemically-weathered phosphorus river flux should increase in response to increased chemical weathering rates, but the relative proportion of DIP, DOP, POP, and PIP may vary and impact the amount of reactive phosphorus entering the ocean. Here we consider possible variations in the phosphorus cycle on two time scales: glacial/interglacial cycles and time periods greater than 1 m.y.

### *Glacial/Interglacial Variations*

By increasing the amount of rock and mineral surface area exposed to chemical weathering, mechanical weathering during glacial periods increases the effectiveness of chemical weathering during the transition to warmer and wetter climates of interglacial periods (Anderson et al., 1997). The effect of increased glaciation over the past 2.5 m.y. is predicted to have increased global silicate weathering by 40% and increased the global river cation flux by as much as 8% (Blum, 1997). Increased chemical weathering rates should increase the reactive phosphorus river flux during interglacials, but the concurrent marine transgression is predicted to increase the phosphorus trapping efficiency of estuaries and shelf areas resulting in more rapid phosphorus burial nearshore than in the deep sea (Ruttenberg, 1993). An increase in shelf area from the rise in sea level during deglaciation will result in an increase in primary productivity over shelf areas (Raymont, 1983). The release of regenerated organic phosphorus on or just below the seafloor enhances precipitation of CFA on the shelf because 25% of phosphorus remineralization occurs in shelf sediments compared to only around 1% in pelagic sediments (Jørgensen, 1983). The amount of shelf area underlying highly productive surface waters is therefore an important control on phosphorite formation and on the rapid removal of reactive phosphorus from the ocean (Arthur and Jenkyns, 1981). Pelagic productivity and the biological CO<sub>2</sub> pump are expected to decrease, and atmospheric pCO<sub>2</sub> is expected to increase during interglacials from less phosphorus input to the deep ocean and less intense upwelling (Broecker, 1982).

The decreased rate of chemical weathering in the transition to cooler and drier global climate of glacial periods is predicted to result in less river input of reactive phosphorus. The lower river phosphorus flux may be offset by a greater phosphorus reflux from resuspension of margin sediments, more direct transport of river sediment to the shelf/slope break, and erosion of older interglacial phosphorus-rich estuarine and shelf deposits. During glacial periods, estuaries and shelf areas are less extensive, and therefore, less of the reactive phosphorus

river flux is trapped nearshore and more of the river load is deposited in deeper water. As sea level drops, the shelf area decreases and primary productivity shifts to areas overlying deeper water. Primary production over deeper water results in more phosphorus regeneration in the water column where reactive phosphorus is returned by upwelling to sustain high surface water productivity and lower levels of atmospheric CO<sub>2</sub>.

The residence time of phosphorus would increase as a consequence of reduced rates of phosphorus input and output (Ruttenberg, 1993). As phosphorus input is reduced towards the minimum values in Table 1A, the residence time approaches 100 kyr making it less likely that variations would be seen on glacial/interglacial timescales. Eolian input also increases during glacial periods as shown in ice core dust records (Petit et al., 1990). The increased dust input further promotes marine productivity by providing phosphorus (Graham and Duce, 1982) and trace elements to surface waters (Berger and Wefer, 1991; Martin, 1991). Trace elements such as iron may in fact be more important than phosphorus in limiting primary production on glacial/interglacial timescales. Greater iron and aluminum inputs during glacial intervals coincide with greater phosphorus concentrations and accumulation rates in two Southern Ocean cores as well as with an increased dust flux in Antarctic ice cores (Latimer and Filippelli, 1997), supporting the possible links between dust, productivity, and nutrient budgets.

Changes in the terrestrial biosphere may also affect the phosphorus flux to the oceans. Interglacial terrestrial carbon storage is estimated to have increased by 750–1050 Gt (10<sup>15</sup>g) over that of glacial periods (Crowley, 1995). The terrestrial biomass is dominated by soil organic matter with an average C/P wt ratio of 154 (Ramirez and Rose, 1992). The change in the average terrestrial phosphorus storage would be 6 × 10<sup>15</sup>g. Uptake or release of this organic phosphorus over a period of 10–20 kyr would result in a significant phosphorus flux of 0.3–0.6 × 10<sup>12</sup>g/yr. The delivery of phosphorus by rivers would be expected to change in response to the terrestrial biomass with a greater flux of POP and DOP relative to iron-bound PIP during interglacials. Uptake of phosphorus by the terrestrial biosphere and trapping of riverine POP in estuaries will act to diminish any increase in the chemically weathered phosphorus flux to the ocean during interglacials.

### *Variations on Geologic (>1 m.y.) Time Scales*

The impact of climate on phosphorus input and oceanic circulation are largely similar to those discussed above for glacial/interglacial cycles but m.y. time scales also include tectonic processes such as MOR spreading rates and associated long-term sea-level fluctuations, variations in uplift and erosion associated with orogenic events, and long-term climate transitions from greenhouse to ice house worlds. The reactive phosphorus input is predicted to be proportional to chemical weathering rates which in turn are related to climate (temperature and rainfall) and mean elevation (tectonism) (Garrels and Mackenzie, 1971; Holland, 1978). Tectonic uplift produces more sediment by mechanical erosion, but does not necessarily

increase chemical weathering rates (Garrels and Mackenzie, 1971). A time lag is likely between particle production on continents by glaciation or orogeny and chemical weathering and delivery to oceans for biological uptake (Föllmi, 1995; Van Cappellen and Ingall, 1996). In the case of the uplift and erosion of the Himalayan-Tibetan Plateau (HTP), for example, monsoon rains appear to be an important factor in increasing chemical weathering rates and phosphorus input (Filippelli, 1997b). Phosphorite formation appears to correlate with periods characterized by increased rates of chemical weathering associated with warm, humid climate (Kazarinov, 1966; Zanin, 1989). However, recent studies indicate that there is no simple relationship between climate and chemical weathering rates. Lithology and degree of physical degradation appear more important than climatic factors (temperature and precipitation) in determining the rate of chemical weathering by  $\text{CO}_2$  uptake (Edmond and Huh, 1997; Allègre et al., 1997).

Geochemical proxies are improving our understanding of possible variations in chemical weathering rates, but the results remain equivocal. The increase in the marine strontium isotope ratio in the last 40 m.y. is interpreted to represent some combination of increased chemical weathering rates and weathering of increasingly radiogenic source rocks (Raymo et al., 1988; Hodell et al., 1990; Richter et al., 1992). Alternatively, the seawater strontium isotope evolution may reflect slowing of MOR spreading rates rather than uplift and erosion of the HTP (Allègre et al., 1997). An increase in Os isotopes in the last 25 m.y. suggests an increase in the weathering of old black shales (Ravizza, 1993), but a decrease in the Ge/Si ratio in the last 30–40 m.y. suggests an overall decrease in the rate of chemical weathering (Shemesh et al., 1989).

The largest primary sink of reactive phosphorus is organic matter. The marine carbonate  $\delta^{13}\text{C}$  record is a potentially useful proxy for variations in organic carbon burial, but interpretation of the  $\delta^{13}\text{C}$  record is complicated by the dependence of  $\delta^{13}\text{C}$  values on the carbonate ion concentration (Spero et al., 1997). Variations in the carbonate ion concentration, related to changes in atmospheric  $\text{CO}_2$  content and ocean chemistry, are sufficient to explain much of the observed variation in the late Pleistocene  $\delta^{13}\text{C}$  record (Spero et al., 1997). In cases where the  $\delta^{13}\text{C}$  record can be used to estimate unambiguously changes in long-term organic carbon burial rates, it is still necessary to distinguish between terrestrial and marine organic carbon, as coal deposits do not provide a sink for marine phosphorus. For example, the large positive  $\delta^{13}\text{C}$  excursion in the late Paleozoic (Carboniferous to early Permian) probably reflects an increase in the formation of coal deposits related to the evolution of vascular land plants (Bernier and Canfield, 1989). The large, middle to late Permian, phosphorite deposits of the Phosphoria Formation appear to be related to a major period of glaciation (Sheldon, 1989) and post date the Carboniferous to early Permian positive  $\delta^{13}\text{C}$  excursion.

Large, reworked phosphorite deposits perhaps proxy for short-term marine organic carbon burial (Compton et al., 1990; 1993). This proxy works by virtue of the rapid decoupling of phosphorus from organic matter during early diagenesis. In addition to phosphorus buried as organic matter, a significant

amount of organic phosphorus is remineralized by microbial activity and taken up by precipitation of authigenic CFA while the organic carbon is returned to the oceans by oxidation during early diagenesis (Fig. 2). The decoupling of phosphorus and organic carbon burial fluxes can occur on time scales smaller than the oceanic residence time of carbon ( $10^5$  yr), so that changes in organic carbon burial are not reflected in the  $\delta^{13}\text{C}$  record. The burial flux of rapidly decoupled phosphorus is predicted to increase during periods of marine transgression and intensified coastal upwelling as productivity shifts to shallow water (shelf) areas where mineralization of phosphorus from organic matter at or below the seafloor is maximized (Jørgensen, 1983). Large phosphorite deposits commonly form on shelf and upper slope areas during marine transgressions and are then reworked by marine regressions. Examples include phosphorite currently forming on the southwest African shelf (Birch et al., 1983; Birch, 1990) and from the Peru-Chile upper continental slope (Glenn et al., 1994a) where upwelling and productivity are particularly strong. Strontium isotope dates of phosphorite grains show that the grains are typically older (by up to several million years) than the sediment in which they occur and indicate extensive reworking of phosphorite deposits (Compton et al., 1993).

Increased MOR spreading rates are expected to increase hydrothermal MOR activity and release of iron-manganese oxyhydroxide particles in plumes to scavenge phosphate from seawater (Wheat et al., 1996). In general, MOR spreading rates have decreased from the middle Cretaceous to the Oligocene and then increased somewhat since the late Oligocene (Kominz, 1984). As phosphate is scavenged by iron oxide particles, the phosphate concentration of the oceans should decrease, thereby providing a feedback to limit the amount of phosphorus scavenged.

The Cretaceous was a period of warm humid climate, high MOR spreading rates, and high sea level. The warm wet climates may have promoted chemical weathering and river input of phosphorus, with 10% greater rainfall estimated for the Late Cretaceous by climate models (Bush and Philander, 1997). A higher phosphorus input may have been offset by increased trapping of phosphorus in estuaries, precipitation of CFA on an expanded shelf area, and scavenging of phosphorus in the water column by iron-manganese oxyhydroxide particles from high MOR spreading rates. The decrease in MOR spreading rates (Kominz, 1984) and the associated decrease in the amount of reactive phosphorus removed by iron-manganese plumes between 100 and 40 m.y. ago may have promoted formation of large Late Cretaceous and early Tertiary phosphorite deposits and increased the organic phosphorus sink by increasing the amount of phosphorus available for biological uptake. Large reworked Late Cretaceous phosphorite deposits (Notholt et al., 1989) together with positive excursions in the marine  $\delta^{13}\text{C}$  record (Schlanger et al., 1987) may also reflect increased short- and long-term marine organic carbon burial. Although Late Cretaceous oceanic circulation rates were perhaps similar to those of today (Bush and Philander, 1997), lower oxygen-renewal rates may have resulted in expansion of oxygen-minimum zones (Schlanger et al., 1987; Arthur et al., 1987) thereby

increasing the total reflux of phosphorus out of sediments into the ocean (Van Cappellen and Ingall, 1994).

In the transition from Eocene to present, climate has become cooler and drier, sea level has dropped, and MOR spreading rates have decreased. The river flux of phosphorus may have increased as a result of uplift and erosion of the HTP (Raymo et al., 1988; Filippelli, 1997b) and increased glaciation (Blum, 1997). A greater phosphorus reflux from sediment resuspension, as well as an increase in reworked CFA, since the late Pliocene are predicted because of high-frequency, high-amplitude sea-level fluctuations concomitant with ice-volume changes. The amount of oceanic phosphorus available for biological uptake and formation of phosphorite deposits would also be enhanced by low MOR spreading rates which reduced the amount of phosphorus scavenged by oxyhydroxides. A positive correlation between sea level and phosphorus accumulation rate from 160 to 32 m.y. ago in the deep sea sediment record is interpreted to result from increased chemical weathering during periods of high sea level. A negative correlation of sea level and phosphorus accumulation rate since 32 m.y. ago may reflect accelerated chemical weathering from increased glacial erosion (Föllmi, 1995).

### Phosphorite Giants

Are large phosphorite deposits ("giants") the result of increased input of reactive phosphorus to the ocean or do they simply represent a focused output of phosphorus from the ocean produced by changes in ocean circulation (large, sustained upwelling sites) and concentrated by later reworking?

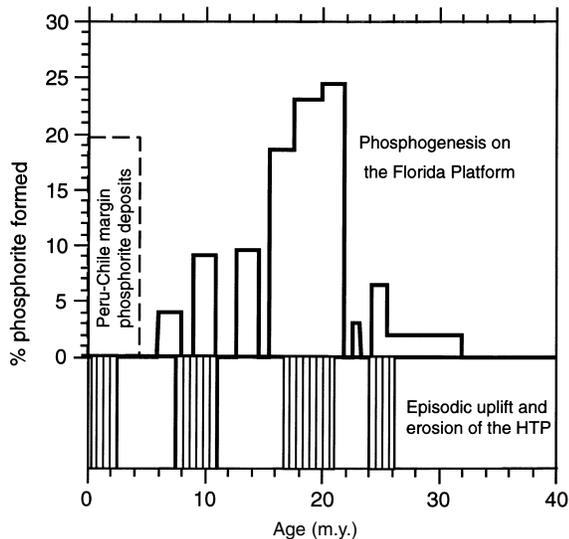


FIG. 3.—Comparison of the timing of proposed periods of increased Himalayan-Tibetan Plateau (HTP) uplift and erosion (Sorkhabi and Stump, 1993) and the timing and relative magnitude of phosphogenesis on the Florida Platform (Compton et al., 1993; Mallinson and Compton, 1997). Percent phosphorite formed is the percent of the total phosphorite on the Florida Platform that formed within the specified age intervals. The vertically hatched areas indicate the proposed time intervals of increased HTP uplift and erosion. Large phosphorite deposits on the Peru-Chile margin (Glenn et al., 1994a) may correspond to increased uplift and erosion of the HTP since 2 m.y. ago.

Phosphorite giants may form when the riverine reactive phosphorus flux exceeds the capacity of the long-term organic matter and particulate iron-oxide fluxes to remove phosphorus from the ocean. Compton and Mallinson (1996) estimate an excess reactive phosphorus river flux to the oceans of between  $9\text{--}23 \times 10^{16}$  moles from the proposed increase in the strontium river flux that is required to explain the strontium isotope evolution of seawater over the last 30 m.y. (Richter et al., 1992). The reactive phosphorus input is assumed to increase in proportion to the strontium increase. The early to middle Miocene rapid increase in the reactive phosphorus river flux predicted by the strontium model corresponds to an episode of major uplift and erosion of the HTP and phosphogenesis on the Florida Platform (Fig. 3). Uplift and erosion of the HTP has been an ongoing process since 50 m.y. ago, but several studies suggest that uplift and erosion were episodic and particularly rapid in the Miocene from 21–16 m.y. ago, from 11–7 m.y. ago, and possibly from 26–24 m.y. ago (Sorkhabi and Stump, 1993). Early to middle Miocene phosphorite on the Florida Platform can account for roughly 20–60% of the excess reactive phosphorus input between 21–16 m.y. ago. Correlation of the relative magnitude and timing between Neogene uplift and erosion of the HTP and phosphogenesis in the southeast USA suggests that phosphorite deposits of the southeast USA and elsewhere may represent, in part, the burial sink of the proposed increased weathering flux of phosphorus from the HTP to the oceans (Compton and Mallinson, 1996). A greater phosphorus sink from organic matter burial or scavenging is not supported by the Neogene marine  $\delta^{13}\text{C}$  record (Shackleton and Hall, 1995) or MOR spreading rates (Kominz, 1984).

Uplift and erosion of the HTP continued after the Miocene with a major episode of uplift and erosion from about 2 m.y. ago to the present. Where are the sinks of the phosphorus derived from HTP erosion during the Pliocene and Pleistocene? Large phosphorite deposits have formed in the last 6 m.y. in the Peru-Chile and Namibian margin areas. The Peru/Chile margin is the site of a Modern phosphorite giant containing an estimated  $140\text{--}746 \times 10^{12}\text{g}$  phosphorus (Glenn et al., 1994a). Phosphatic sediment recovered from the Peru margin suggests that this area has been a major phosphogenic province since at least the late Miocene (Garrison and Kastner, 1990). The present-day burial flux of phosphorus as phosphorites on the Peru margin is comparable to that of the Miocene southeast USA burial flux of  $0.06\text{--}0.4 \times 10^{12}\text{g/yr}$  (Mallinson and Compton, 1997). Combined with phosphorite formation on the southwest African shelf as well as an apparent increase in the pelagic phosphorus burial rate from 10 m.y. ago to the present (Föllmi, 1995), appears sufficient to remove the present-day excess phosphorus flux from erosion of the HTP. Alternatively, the phosphorus weathering flux from the HTP may have decreased since the late Pliocene because of an increase in mechanical weathering and decrease in chemical weathering with glaciation (Filippelli, 1997b).

### SUMMARY

The pathway of phosphorus from chemical weathering on

the continents to final burial in marine sediments is complex and not well understood. The maximum prehuman potentially reactive phosphorus flux to the ocean is estimated to be  $3.1\text{--}4.8 \times 10^{12}\text{g/yr}$ ; the minimum flux could be as low as  $0.7 \times 10^{12}\text{g/yr}$  depending on the amount of phosphorus released from iron-bound PIP, the fate of dissolved and particulate organic phosphorus, and the influence of estuaries as phosphorus traps. Variations in the rate of burial of primary phosphorus bound to MOR-derived iron-oxide particles can be inferred from MOR spreading rates. Variations in burial rate of phosphorus associated with organic matter are more difficult to evaluate because of the dependence of the  $\delta^{13}\text{C}$  record on ocean chemistry and on the amount of terrestrial as well as marine organic carbon burial. Much of the organic matter phosphorus and iron-bound PIP is redistributed during early diagenesis to CFA and iron oxides. The use of authigenic CFA as an indicator of the burial flux of reactive phosphorus is complicated by the fact that phosphorus in CFA is also derived from detrital iron-bound PIP (sink switching) and the presence of river-borne (detrital) CFA, particularly in shelf areas adjacent to rivers. Estimated phosphorus output ( $1\text{--}2.5 \times 10^{12}\text{g/yr}$ ) is less than the phosphorus input flux and suggests that 12–40% of the iron-bound PIP (adsorbed phosphorus) flux is released to the ocean. The uncertainty in the input and output fluxes is large, but could improve with more data on the amount and nature of iron-bound PIP, and the amount of iron-bound phosphorus released by desorption when freshwater mixes with seawater and during sediment resuspension.

The phosphorus cycle has most likely varied in the past in response to changes in chemical weathering rates (climate and orogeny), sea-level fluctuations, MOR spreading rates, glaciation, and oceanic circulation. Major periods of orogeny and glaciation appear to enhance phosphorite formation by increasing the chemical load of rivers. Phosphorite giants are more likely to form during marine transgressions that coincide with increased chemical weathering rates (warm and humid climate combined with increased physical weathering) and less MOR hydrothermal activity. As sea level rises, upwelling and primary productivity shift to expanded shallow-water estuary and shelf areas where a greater portion of the organic phosphorus is released and captured by CFA or iron oxides on or just below the seafloor rather than being recycled in the water column. Shelf deposits are then susceptible to reworking by sea-level fluctuations. A significant but unknown amount of CFA may form by rapid ( $<10^5$  yrs) remineralization of organic matter. Large, phosphorite deposits may provide a proxy for short-term organic carbon burial and a sink of phosphorus when phosphorus input exceeds the long-term organic carbon and MOR iron-oxide burial sinks.

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