

THE MARINE PHOSPHORUS CYCLE

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ABSTRACT. Phosphorus introduced to the ocean must ultimately be removed if a steady state is to be maintained over geologic time. Aeolian input is insignificant, and there is evidently no hydrothermal contribution. Rivers dominate P-input to the ocean. The fluvial P-flux is poorly quantified due to the interactions of two factors: (1) man's influence on river-nutrient fluxes, and (2) inherent complexities in understanding the biological and inorganic associations of P in estuarine and coastal waters. Our "best estimate" of the natural or pre-man P-input flux is about 10×10^{-9} moles $-P/cm^2$ -ocean surface/year.

Of the identified flux of phosphorus to the sediments, about 90 percent is in the form of biogenic debris or its regeneration products: (1) organic-rich hemipelagic sediments with a P_{org}/C_{org} mole ratio of about 4×10^{-3} ; (2) biogenic calcium carbonates containing several hundred ppm-P ($P_{Co_3}/C_{Co_3} = 1 \times 10^{-3}$), apparently mostly in coccoliths; and (3) authigenic phosphorites, which are marginally significant in today's ocean. P-removal with (4) metalliferous sediments on hydrothermally-active ridge crests may be an additional minor sink. The burial of phosphatic fish debris is negligible. P-removal by direct reaction of phosphate in seawater with sea-floor basalts during mid-ocean ridge hydrothermal circulation is insignificant. P-removal by processes such as sorption on clay surfaces or formation of authigenic Fe and Al phosphate phases is presently unquantified and remains a serious uncertainty in the phosphorus cycle.

The identified sources and sinks approximately balance, yielding a residence time for P in the oceans of about 10^5 yrs.

INTRODUCTION

Phosphorus is an essential nutrient for primary productivity in the oceans. However, the dependence of productivity on the phosphorus flow through the ocean is unknown. The exact response of productivity is undoubtedly very complex due to fixed-N limitation, luxurious consumption, and changes in oceanic ecology. Thus primary production rates may not be linearly related to the flow of phosphorus through the oceans, and biological processes in the oceans might not change much if the phosphorus content of the deep sea were 10 or 20 percent higher or lower than the present values. There is little doubt, however, that large variations in

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the phosphorus content of the deep oceans (upon which supply to the euphotic zone depends, via upwelling) would dramatically affect primary production and many nutrient-sensitive ecological relationships.

Until recently, there was little systematic quantitative data regarding the crucial question of how phosphorus is removed from the oceans. The primary purpose of this paper is to present new evidence concerning the sinks of phosphorus from the ocean and to incorporate this evidence into our understanding of the P-cycle. We will first discuss potentially important input fluxes, attempt to estimate (again) the fluvial flux, and discuss the problems of estuarine and coastal processes that modify the fluvial flux to the deep sea. We will then briefly review the arguments concerning the ultimate controls of the deep-sea phosphorus concentration and attempt to quantify P-fluxes out of the oceans. The final result will demonstrate that processes controlling the deep-sea phosphate concentration are related to several biologically and sedimentologically-linked processes.

INPUTS OF PHOSPHORUS TO THE OCEAN

If oceanic phosphorus is in steady-state, then the burial of phosphate in sediments must be balanced by inputs. Potentially important input pathways of phosphorus to the oceans include continental low-temperature weathering (fluvial and aeolian fluxes), high-temperature submarine hydrothermal "weathering," and submarine low-temperature seawater-basalt exchange. The atmospherically transported, sea-water-soluble P-flux from the continents to oceans is poorly known but is evidently considerably less than 10 percent of the fluvial flux and will be ignored here (Graham and Duce, 1979). We present below estimates of input fluxes against which the burial fluxes we compute later may be compared.

Hydrothermal input.—Mid-ocean ridge hydrothermal processes (Corliss and others, 1979; Edmond and others, 1979a, b) would produce a flux of soluble-P to the oceans, if phosphorus were solubilized from sea-floor basalt and carried into the oceans by P-enriched hydrothermal seawaters. The stratigraphic proximity of many phosphate deposits to volcanogenic deposits is consistent with this hypothesis (Riggs, 1980). If so, then the P-enrichment of metalliferous sediments may derive directly from hydrothermal solutions (see Sheldon, 1981; Baturin, 1978; Koritnig, 1970), rather than by scavenging from seawater with hydrothermally-derived iron precipitates (Berner, 1973; Froelich, Bender, and Heath, 1977; Bloch, 1978; see below). Two pieces of evidence argue against this hydrothermal input hypothesis. First, P-analyses of model high-temperature seawater-basalt reactions at 400°C (the presumed high-temperature endmember: Edmond and others, 1979) yielded P-concentrations of only 13 μM (Froelich, Bender, and Heath, 1977). Since the global hydrothermal water flux is about 0.5 percent that of the global river water flux, and since rivers contain about 1 $\mu\text{M-P}$ (see below), the hydrothermal input could only be about 7 percent of the fluvial input. Most of this would presumably end up in metalliferous sediments rather than dissolved in seawater, so the net input to the oceans would be negligible in any case. Secondly, data

from "cool" vents (Galápagos II, see fig. 7) suggests that P is depleted in the hydrothermal effluent rather than enriched. There are two reasonable explanations for this observation: (1) P is removed from seawater by reaction with basalt at high temperatures, or (2) P is leached from basalt at high temperatures and thus enriched in the fluid but is then removed from hydrothermal solutions by low temperature secondary reactions occurring within the vent plumbing (Edmond and others, 1979b). If the former is correct, then MOR hydrothermal processes are a sink rather than a source of P. If the latter is correct, then we cannot discern the high-temperature endmember (and thus the P-flux) from "cool" vent data. Direct evidence from "hot" vents and the accumulated mineral assemblages is needed to answer this question. Preliminary data from the 21°N East Pacific Rise black smoker vents suggest that P is depleted in the high temperature endmember (Edmond, personal commun.). Thus it appears that hydrothermal circulation of seawater through the crust is not a source of P and may in fact be a small (insignificant) sink.

Low-temperature weathering input.—Phosphorus could enter the oceans via low-temperature reactions between seawater and sea-floor basalts. In order to enter the oceans, phosphorus released during such reactions must diffuse through the pore waters of the overlying sediment pile. If low-temperature exchange is a significant source of P to the oceans, the P-flux from basement to seawater through pore water must be comparable to the fluvial P-flux (10×10^{-9} mole $\text{—P cm}^{-2}\text{yr}^{-1}$). Assuming pure Fickian diffusion and taking a diffusion coefficient for phosphate of $3.6 \times 10^{-6}\text{cm}^2\text{sec}^{-1}$ (Krom and Berner, 1980b), then the gradient necessary to drive this flux can be estimated:

$$F_p = D_p \frac{d(\text{PO}_4)}{dz}$$

where F_p = diffusive P-flux $\sim 10 \times 10^{-9}$ mole $\text{cm}^{-2}\text{yr}^{-1}$

D_p = diffusion coefficient of P $\sim 3.6 \times 10^{-6}\text{cm}^2\text{sec}^{-1}$

$\frac{d(\text{PO}_4)}{dz}$ = P = pore water gradient with depth in sediment

$$\frac{d(\text{PO}_4)}{dz} = \frac{F_p}{D_p} \approx 10 \mu\text{mole l}^{-1}\text{m}^{-1}$$

There is no evidence to support the existence of such large positive gradients in basal sediments. The few DSDP phosphate pore water profiles in fact show negative gradients near the sea floor (fig. 1; Cook, 1974; Gieskes, 1973). In addition, comparison of P-contents of altered (weathered) sea-floor basalts with fresh (unweathered) ridge-crest tholeiitic basalts suggests that basalts gain P during low-temperature reactions (Hart, 1970). Thus, low-temperature basalt reactions do not appear to be a P-source.

Fluvial input.—Attempts to estimate the fluvial flux of "reactive" phosphorus encounter at least four problems: (1) it is unknown what fraction of the total phosphorus eroded from the continents is solubilized,

that is, we do not know what controls the dissolved phosphorus concentrations of rivers; (2) we do not know the extent (or even the direction!) to which the riverine P-flux is modified in estuaries; (3) man's tremendous influence on the present phosphorus flux through deforestation and use of fertilizer precludes estimating the "pre-agricultural" dissolved phosphorus flux directly from most of the contemporary river data; and (4) some of the riverine particulate phosphorus flux (including an anthropogenic component) may dissolve (or desorb) and become geochemically (biologically) "reactive" once in the oceans. We will estimate the natural P-flux, keeping these uncertainties in mind.

The total phosphorus flux to the oceans can be estimated from present and pre-agricultural total continental denudation rate estimates (Judson, 1968; Gregor, 1970) (table 1). If the total phosphorus content of the Earth's crust were eroded uniformly and carried to the oceans, the total (dissolved plus particulate) pre-agricultural phosphorus flux would be about 90×10^{-9} moles $\text{cm}^{-2}\text{yr}^{-1}$, on a whole ocean basis. (All fluxes in this paper are given in units per cm^2 of ocean area.) Man's acceleration of the denudation process alone (through deforestation, cultivation, and urbanization) has increased this total flux to about 210×10^{-9} moles-P $\text{cm}^{-2}\text{yr}^{-1}$. In addition to increased continental erosion, man directly mines an additional 130×10^{-9} moles-P $\text{cm}^{-2}\text{yr}^{-1}$, primarily for fertilizers. On a short term basis, this phosphorus is tied up in subsoil horizons of agricultural land, but in the long run, it must find its way eventually to the sea. It is not clear whether man's fertilization of agricultural lands will lead to an increase in the input of reactive-P to the

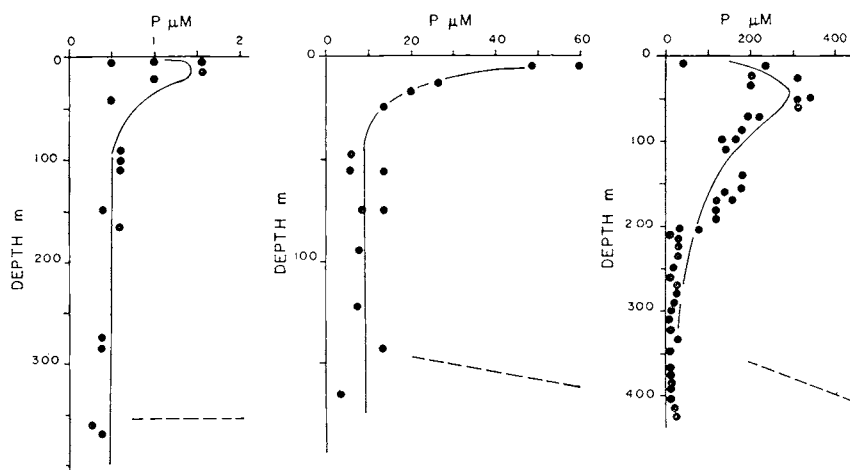


Fig. 1. Interstitial phosphate gradient in DSDP holes approaching basement: (A) DSDP site 149, Venezuela Basin, Caribbean Sea (Gieskes, 1973); (B) DSDP site 147, Cariaco Tranch, Caribbean Sea (Gieskes, 1973); (C) DSDP site 262, Timor Trough, southwestern Pacific Ocean (Cook, 1974). The curves drawn through the data are model fits from Toth and Lerman (1977). Dashed line near basement is the approximate phosphate gradient that would be necessary to drive an upward flux of P derived from basalt to equal the P influx to the oceans from rivers: $d\text{PO}_4/dz = 10 \mu\text{mole l}^{-1} \text{m}^{-1}$.

TABLE 1
Total phosphorus fluxes to the oceans

	<u>Pre-agricultural phosphorus flux</u>	
Pre-agricultural total continental denudation rate	$10 \times 10^{15} \text{ g yr}^{-1}$	Judson, 1968
Phosphorus concentration of the Earth's crust	0.1%	Gregor, 1970 McKelvey, 1973
<u>Total pre-agricultural river phosphorus flux</u>	$100 \times 10^{11} \text{ g yr}^{-1} = 90 \times 10^{-9} \text{ moles-P cm}^{-2} \text{ yr}^{-1}$	
	<u>Contemporary phosphorus flux</u>	
Total river suspended load	$18.3 \times 10^{15} \text{ g yr}^{-1}$	Holeman, 1968
Total river bedload	$1.8 \times 10^{15} \text{ g yr}^{-1}$	Judson, 1968
Total river dissolved load	$3.8 \times 10^{15} \text{ g yr}^{-1}$	Livingstone, 1963 Gibbs, 1967
Total continental denudation rate	$24 \times 10^{15} \text{ g yr}^{-1}$	
Phosphorus concentration of the Earth's crust	0.1%	McKelvey, 1973
<u>Total contemporary phosphorus flux</u>	$240 \times 10^{11} \text{ g yr}^{-1} = 210 \times 10^{-9} \text{ moles-P cm}^{-2} \text{ yr}^{-1}$	
	<u>Man-mined potential phosphorus flux</u>	
Phosphate rock mined by man (in 1980)	$11 \times 10^{13} \text{ g yr}^{-1}$	extrapolated from Emigh, 1973
Average phosphorus content of mined phosphate rock	13.3%	Stumm, 1973
<u>Potential total phosphorus flux by man's mining of P</u>	$145 \times 10^{11} \text{ g yr}^{-1} = 130 \times 10^{-9} \text{ moles cm}^{-2} \text{ yr}^{-1}$	

TABLE 2
Dissolved phosphorus river flux estimates

Phosphorus flux 10^{-9} moles $\text{cm}^{-2}\text{yr}^{-1}$	Reference	Basis
	I. <u>Contemporary</u>	
18	Rittenberg, Emery, and Orr, 1955	Contemporary river flux estimate including man's input
17	Stumm, 1973	Solubility of apatite + 50% man's influence including man's input
15	Lerman, McKenzie, and Garrels, 1975 Garrels, MacKenzie, and Hunt, 1975	From Garrels and MacKenzie (1971), probably including man's input
5	Silker, 1964	Contemporary Columbia River ($\sim 0.6 \mu\text{M}$ dissolved-P)
14	Williams, 1968	Amazon River (total-P $\approx 50 \mu\text{g l}^{-1}$) Total P \approx Dissolved Org + Reactive
	II. <u>Pre-agricultural</u>	
3.6	Froelich, Bender, and Heath, 1977	Amazon River (Gibbs, 1972: dissolved-P = $13 \mu\text{g l}^{-1}$)
6.2	Riley and Chester, 1971 Goldberg and others, 1971	Average rivers = $20 \mu\text{g l}^{-1}$ (Pre-agricultural)
7.1	Holland, 1972	(Pre-agricultural)
3.6	Ronov and Korzina, 1960	(Pre-agricultural)

oceans. This potential acceleration of the phosphorus cycle has been discussed by Stumm (1973) and Lerman, MacKenzie, and Garrels (1975).

The "reactive" flux is more difficult to estimate, since it includes not only dissolved reactive phosphate but also dissolved organic phosphorus plus any potentially dissolvable forms, such as phosphate adsorbed to clays and iron oxides, iron, and aluminum phosphates, and any particulate organic phosphorus, some portion of which may be released in seawater and enter the biological cycles. Estimates of the relative importance of these fractions in contemporary rivers cannot be easily extrapolated to pre-agricultural fluxes.

We can try to set limits on the "reactive" phosphorus river input. First, we can safely assume that much less than 100 percent of the total pre-agricultural phosphorus flux is reactive in the oceans, so that the maximum upper limit is about 90×10^{-9} moles-P $\text{cm}^{-2}\text{yr}^{-1}$. Contemporary dissolved phosphorus river flux estimates generally range from 14 to 18×10^{-9} moles-P $\text{cm}^{-2}\text{yr}^{-1}$ (table 2), which we might take as a more reasonable upper limit, although often it is not clear whether some of these estimates include reactive fluvial forms other than dissolved phosphorus. As a reasonable lower limit, we can use estimates of the pre-agricultural dissolved phosphorus flux based on observed concentrations in "undisturbed" rivers (for example, the Amazon) or on apatite solubility arguments. These values range from 3.6 to 7.1×10^{-9} moles-P $\text{cm}^{-2}\text{yr}^{-1}$.

Table 3 summarizes these upper and lower estimates of the river flux. The wide range of these values exemplifies the difficulties inherent in attempting to estimate the fluvial flux. We will nevertheless select a value of about $10 \pm 5 \times 10^{-9}$ moles $\text{cm}^{-2}\text{yr}^{-1}$ (P rivers $\cong 1 \mu\text{M}$) as an "acceptable" value for the river flux and emphasize that this may be a chimera.

Input from estuaries and shelves.—The fluvial flux of phosphorus is delivered to the ocean via estuaries and coastal waters. The fluvial dissolved flux can be modified here in three ways: (1) adsorption/desorption of reactive-P onto/off-of surfaces of river-borne suspended clays, (2) biological uptake by estuarine organisms or release of reactive-P from dissolved

TABLE 3
Estimates of natural (pre-agricultural) "reactive" phosphorus river flux

	Flux		Normalized to ocean area ($3.62 \times 10^{18} \text{ cm}^2$)	Normalized to river water flux ($3.3 \times 10^{10} \text{ l}$)
	$10^{11} \text{ moles yr}^{-1}$	$10^{12} \text{ g P yr}^{-1}$	$10^{-9} \text{ moles cm}^{-2}\text{yr}^{-1}$	μM
Maximum Upper limit	3.2	10	90	10
Reasonable Upper limit	0.5-0.6	1.5-1.9	14-18	1.5-2.0
Reasonable Lower limit	0.1-0.3	0.3-0.9	4-8	0.4-0.8
"Acceptable" value	0.4 ± 0.2	1.2 ± 0.6	10 ± 5	1 ± 0.5

or particulate organic matter produced upstream, and (3) the transformation (via slow dissolution, desorption, and regeneration) of particulate unreactive-P (transported by rivers to estuaries and shelf sediments) to reactive, dissolved-P, followed by its eventual release to the overlying water.

Several studies of phosphorus behavior in estuaries strongly suggest that rapid desorption reactions with suspended material "buffers" reactive-P at concentrations of about $1\ \mu\text{M}$ over much of the salinity mixing range (Pomeroy and others, 1965; Stefansson and Richards, 1963; Butler and Tibbitts, 1972; Parker and others, 1972; Liss, 1976). Data of Froelich and Wells (in preparation) in a local, well-defined, pristine estuary is typical of previous data displaying this "buffering" effect (fig. 2). The popular interpretation is that reactive-P is desorbing from suspended fluvial solids to provide the input necessary to boost concentrations above the theoretical mixing line. The question we must answer is: what is the origin of this input? If really derived from fluvial suspended material, then this mechanism increases the reactive-P flux to the oceans. If derived from marine sources (for example, from marine C_{org} or from marine CaCO_3 swept into the estuary by estuarine circulation along the bottom), then it does not enhance the fluvial P-flux. These preliminary data suggest that, in the Ochlockonee at least, there is insufficient fluvial particulate phosphorus to be the source of this input. If this is true of other

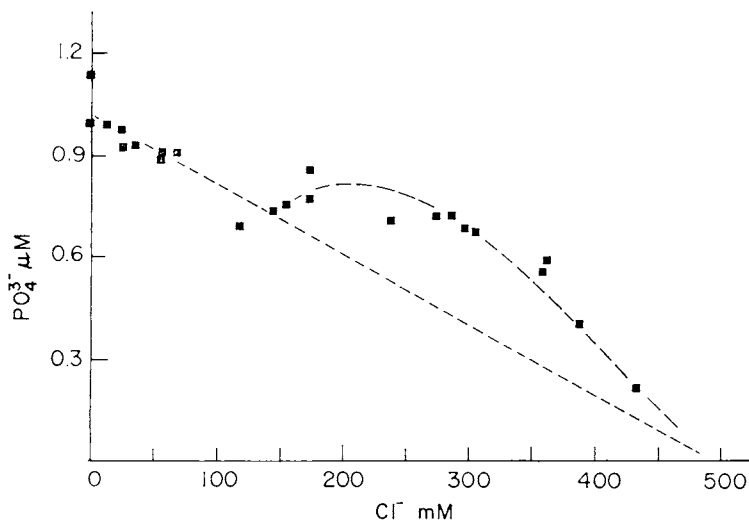


Fig. 2. Dissolved reactive phosphate data in the Ochlockonee River, FL (Oct. 4, 1980) showing typical mid-estuary desorption input, or "buffering." The lower dashed line represents the conservative mixing line between river water and seawater. The upper dashed line shows the approximate input above conservative mixing necessary to explain the observed data. Nitrate and silica data for this date (not shown) followed simple linear mixing lines between river water and seawater end members: there was little biological input or removal. Riverine particulate material contained insufficient reactive-P to provide the input signal observed in the estuary. The simplest explanation of these data is release of P from marine-derived particulate material entrained into the estuary (Froelich and Wells, in preparation).

estuarine systems where "buffering" has been observed, then estuarine input via desorption, dissolution, or regeneration does not enhance the eventual fluvial reactive-P flux to the oceans. A great deal more comprehensive estuarine nutrient work (in pristine systems!) is needed to clarify this supposition.

Biological uptake of P in estuaries and coastal waters is an important potential removal mechanism. Typical data demonstrating such uptake in an estuary is shown in figure 3. Again, the question we must answer is: what is the ultimate fate of the particulate organic-P produced? In the short-term ($\sim 10,000$ yrs = one interglacial high-stand of sealevel), some fraction of the organic-P not rapidly regenerated will be buried in estuarine and shelf deposits and thus deprive the oceans of that fraction of the fluvial input. In the long-term, however ($> 100,000$ yrs = one complete glacial/interglacial rise and fall of sealevel), the P_{org} deposited on shelves will be eroded from the exposed continental shelf and transported to the deep sea. Thus the long-term effect on the fluvial P-flux is nil. It has been argued, however, that this alternating shelf deposition/by-passing of the fluvial P-flux may have measurable consequences for oceanic nutrient-related chemistries on time-scales less than 100,000 yrs (for example, biogenic calcite production and the calcite compensation depth: Broecker, 1971; atmospheric CO_2 : Broecker, 1973, 1981).

For lack of better evidence, then, we will argue that the fluvial P-flux enters the ocean substantially unmodified by estuarine and near-shore

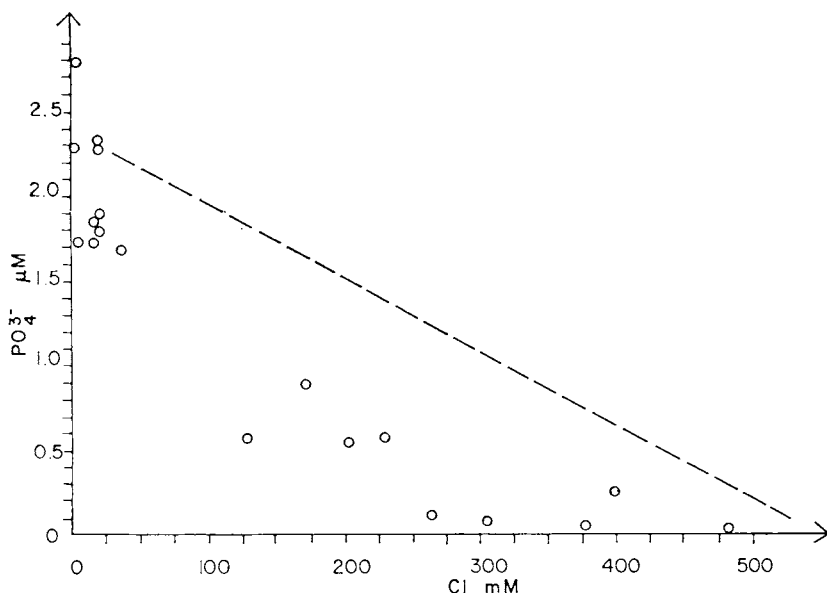


Fig. 3. Dissolved reactive phosphate data in the Ochlockonee River, Florida (May 13, 1980) showing typical biological removal. Biological uptake inferred by high chlorophyll *a* and uptake of NO_3^- and Si (data not shown) in the mole ratios N:P:Si = 16:1:23, characteristic of estuarine diatom blooms (Froelich and Wells, in preparation).

processes, at least on time scales comparable to those of the residence time of P in the oceans (10^5 yrs). Since no other significant input fluxes can be recognized, we take the total input flux of reactive-P to the oceans as equal to the fluvial flux ($10 \pm 5 \times 10^{-9}$ moles $\text{cm}^{-2}\text{yr}^{-1}$). This "best estimate" of the input flux is a guide against which later estimates of various burial fluxes may be compared.

CONTROLS ON THE PHOSPHORUS CONCENTRATION OF THE DEEP SEA

Many have debated whether the maximum deep-sea phosphate concentration is thermodynamically or kinetically controlled. The present phosphate concentration of the deep Pacific is about $3 \mu\text{M}$, which, as Sillén (1967), Pytkowicz and Kester (1967), Atlas (ms), and Atlas and Pytkowicz (1977) have pointed out, is near the value predicted by equilibrium with apatite. Equilibrium models of seawater have, therefore, emphasized that the phosphorus concentrations of deep waters is controlled by apatite solubility (Gulbrandsen and Roberson, 1973) and should be independent of changes in productivity, oceanic mixing, or input/output rates. These models would imply (but not require) that the primary phosphorus sink be associated with inorganic precipitation of apatite from seawater. Francolite, the mineralogical form of marine apatite (McConnell, 1973) displays a wide range in solubility due to its variable chemistry (Atlas and Pytkowicz, 1977), so that it is in fact presently unclear whether the deep Pacific is saturated with respect to any single common marine phosphate salt. In any case, inorganic homogeneous precipitation of calcium phosphate in the water column is apparently kinetically unlikely, requiring several millions of years (Atlas, ms, p. 90). In addition, interstitial phosphate concentrations of both pelagic and hemipelagic sediments likely containing calcium phosphates are generally higher than the local bottom water (Brooks, Presley, and Kaplan, 1968; Baturin, 1972; Hartmann and others, 1973, 1976; Bray, Bricker, and Troup, 1973; Emerson and others, 1980; Jahnke, 1980 and unpub. data; and others). These observations suggest that the deep-sea phosphate concentration is not fixed by simple equilibrium with a single salt.

Kinetic models of seawater chemistry (for example, Redfield, 1958; Broecker, 1971) emphasize the role of non-equilibrium biological processes occurring in the euphotic zone. In such models, the phosphorus concentration of the deep sea is controlled by the interaction of biological processes and oceanic mixing: negative feedback fixes the phosphate concentration of the deep sea at that level necessary to provide the requisite phosphate via upwelling to produce a particulate biogenic phosphorus flux to the deep sea from which is buried a fraction sufficient to balance exactly the river input (Broecker, 1974). If this model is correct, then the major phosphorus sink is biogenic, and the primary control of the deep-sea phosphate concentration involves a balance between burial and regeneration (or dissolution) of biogenic phosphorus.

PHOSPHORUS SINKS

Five processes have been mentioned as potentially important phosphorus sinks (Froelich, Bender, and Heath, 1977): (1) burial of phosphorus tied up in organic matter; (2) sedimentation of biogenic calcium carbonate containing several hundred ppm phosphorus; (3) burial of phosphorus in phosphorites (in sediments underlying highly productive surface waters); (4) burial of phosphatic fish debris; and (5) inorganic sorption and precipitation of phosphate with clays, with iron hydroxyoxides in metalliferous sediments, and with Al and Fe phosphates.

In the following discussion, we will attempt to quantify P-fluxes out of the oceans associated with each of these sinks. In several cases (for example, clay sorption), little pertinent information exists by which we might estimate burial fluxes. Thus our approach here is to document those sinks we can identify and quantify and point out where additional work is needed.

I. Phosphorus Removal With Organic Carbon

Phosphorus is intricately involved with marine productivity, so it is reasonable to suppose that phosphorus removal might occur by burial of organic phosphorus in association with organic matter in sediments. A knowledge of the average $(P:C)_{org}$ ratio buried in marine sediments would permit us to calculate P_{org} -burial from knowledge of the carbon cycle.

During productivity at the sea surface, carbon and phosphorus are fixed into organic matter containing an average $(P:C)_{org}$ mole ratio of 9.4×10^{-3} (the "Redfield ratio", $(P:C)_{org} = 1:106$; Fleming, 1940; Redfield, Ketchum, and Richards, 1963). Most of this organic matter is regenerated either in the upper water column (Bishop and others 1977; Bishop and others, 1980) or on the bottom (Müller and Suess, 1979). A small fraction of the organic productivity at the sea surface escapes the upper ocean in fecal pellets and other large aggregates that sink rapidly to the sea floor. These "fast flux particles" likely carry the unadulterated surface-water particulate $(P:C)_{org}$ ratio directly to the sediment floor, since there is little chance for regeneration in the water column (Honjo, 1978; Knauer, Martin, and Bruland, 1979; however, see Suess and Müller, 1981). The fine fraction of organic particulates suspended in seawater below the euphotic zone (which does not contribute significantly to the vertical flux) represents "floating" refractory material (residue of regeneration). The $(P:C)_{org}$ ratios in this relict material are typically lower than the Redfield ratio and decrease with depth reflecting fractional regeneration of organic-P from organic-C with "age" of the water (Copin-Montegut and Copin-Montegut, 1972, 1978; Ketchum, Corwin, and Yentsch, ms; Lemasson, Cremoux, and Montel, 1977; Bishop, Edmond, and others, 1977; Bishop, Collier, and others, 1980). Thus the $(P:C)_{org}$ ratio input to the sediment surface is probably close to the Redfield ratio. This need not necessarily be the burial ratio, however, as is often assumed.

To estimate the $(P:C)_{org}$ burial ratio we have plotted the available data for sedimentary C_{org} and $(P:C)_{org}$ (fig. 4). $(P:C)_{org}$ ratios in organic-

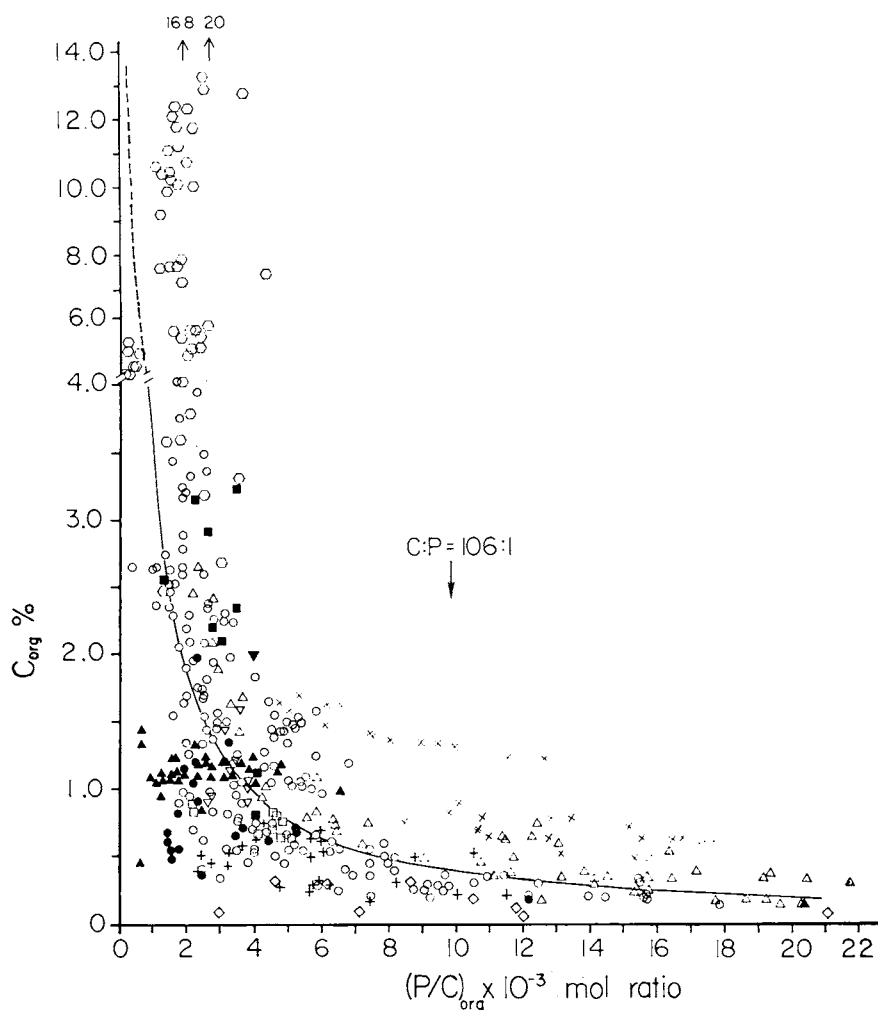


Fig. 4. Percent C versus $(P/C)_{org}$ ratio for sediment data. The Redfield ratio is given by arrow (9.4×10^{-3}). The solid line through the data fits the hyperbolic equation $(\% C_{org}) \times (P/C)_{org} = 4 \times 10^{-3}$, or $p \approx 100$ ppm. Data from \circ northwest African continental rise > 500 m (Hartmann and others, 1976); \bullet northwest African continental shelf and slope < 500 m (Hartmann and others, 1976); \triangle west African continental rise and French equatorial Atlantic > 500 m (Froelich, ms); \blacktriangle west African continental shelf and slope < 500 m (Froelich, ms); \times eastern tropical Pacific MANOP sites "M" (metalliferous) and "H" (hemipelagic) (Froelich, ms); \square western subtropical Atlantic > 2000 m (Cook, ms); \blacksquare east North American continental slope and rise < 2000 m (Cook, ms; Morse and Cook, 1978); $+$ Texas shelf, Gulf of Mexico (Filipek and Owen, 1980); \blacktriangledown Santa Barbara Basin (Sholkovitz, 1973); \triangledown Long Island Sound (Krom and Berner, 1981); \circ Peru continental margin < 650 m (Suess, 1981); \diamond Central Pacific gyre (Suess and Müller, 1981).

rich sediments (> 1 percent C_{org}) are about one-half to one-fifth of the Redfield ratio. This is usually interpreted as reflecting fractional regeneration of P_{org} from C_{org} during oxidation of organic matter in marine sediments (Sholkovitz, 1973; Hartmann and others, 1973; Froelich, ms; Filipek and Owen, 1980). $(P:C)_{org}$ ratios in organic-poor pelagic sediments (< 0.5 percent C_{org}) are, however, apparently enriched in P with respect to the Redfield ratio (Hartmann and others, 1973, 1976; Froelich, ms; Suess and Müller, 1980). This observation may reflect the presence of stable, phosphorus-rich organic moieties that are preferentially enriched during oxic diagenesis of slowly-accumulating pelagic sediments, for example, the inositol phosphates, known to comprise a significant fraction of the P_{org} in soils and lake sediments (Weimar, ms) and recently identified in marine sediments (White and Miller, 1976). An alternate explanation is that organic-poor pelagic sediments contain a larger fraction of biomass carbon, reflecting a bacterial P/C of about 24×10^{-3} (Suess and Müller, 1980).

The curve drawn through the data in figure 4 is a hyperbola satisfying the relationship $(P/C)_{org} \times C_{org} = 4 \times 10^{-3}$. The data are consistent with this inverse relationship (particularly considering the probable scatter introduced by the variety of analytical techniques represented here for the analysis of organic carbon and organic phosphorus in marine sediments). The simplest explanation for this distribution is that the organic phosphorus concentrations of a wide variety of marine sediments are fairly constant at 100 ppm and thus not a function of organic carbon content. Inspecting the data, we find that over 80 percent of the P_{org} data cluster within a factor of two of 100 ppm- P_{org} (50-200 ppm). The outliers consist of two special populations (Froelich, 1979a, b); (1) upper continental slope and shelf cores on the west African continental margin which are known by $\delta^{13}C$ analyses to contain about 20 percent terrestrial organic carbon ($P:C \sim 1.2 \times 10^{-3}$ in "average" terrestrial biomass, Deevey, 1973); (2) metalliferous sediments from the East Pacific Rise which contain high concentrations of labile inorganic-P compounds which might interfere positively in the P_{org} analytical technique.

With these two exceptions, almost all the available sedimentary P_{org} data will fall in the narrow range of 50 to 200 ppm regardless of C_{org} contents in the range from 0.15 to over 4.0 percent. This result is surprising but must ultimately be the result of counterbalancing mechanisms that control the ultimate carbon content (overlying productivity and sedimentation rate: Müller and Suess, 1979; Heath, Moore, and Dauphin, 1977) and $(P:C)_{org}$ ratio (extent of diagenesis?), so that the P_{org} content of marine sediments does not vary widely.

We can estimate the burial rate of organic phosphorus in sediments from the P:C ratio being buried and the burial rate of organic carbon. The long-term (pre-agricultural) burial rate of organic carbon can be calculated from the average river water bicarbonate concentration (0.55 mM, Wedepohl, 1971; corrected for atmospheric cycling) and the world river flow (3.3×10^{16} l yr⁻¹). Assuming that 80 percent of the carbon

entering the oceans is buried as CaCO_3 and 20 percent as organic carbon (Li, 1972; Broecker, 1974; Garrels and Perry, 1974), then the organic carbon burial rate is about 0.99×10^{-6} moles-C $\text{cm}^{-2}\text{yr}^{-1}$ (compare 0.91×10^{-6} moles-C $\text{cm}^{-2}\text{yr}^{-1}$; Garrels and Perry, 1974).

Since over the long-term organic carbon burial occurs primarily in hemipelagic continental-rise sediments (Walker, 1974), and since these sediments and their continental sedimentary counterparts contain between 1.0 and 1.7 percent C_{org} (Clarke, 1924; Ronov and Yaroshevsky, 1969; Parker, 1967), we can take the average P:C value for hemipelagic sediments from figure 4 as about $4 \pm 2 \times 10^{-3}$ (P:C \cong 0.4:106). This value is in agreement with Hartmann and others' (1976) finding that sediments accumulating on continental rises at rates between 6 and 11 $\text{cm } 10^{-3} \text{ yr}^{-1}$ display ratios between 0.44:106 and 0.22:106. {We recognize that some unknown, but potentially significant, proportion of C_{org} burial may be occurring in deltas which are poorly represented in the data compiled in fig. 4.}

Taking the P:C value as 4×10^{-3} and organic burial as 0.99×10^{-6} moles-C $\text{cm}^{-2}\text{yr}^{-1}$, we calculate an organic phosphorus burial rate of about 4×10^{-9} moles-P $\text{cm}^{-2}\text{yr}^{-1}$ or about 40 percent of the estimated P-input to the oceans.

II. Phosphorus Removal with Phosphorites

The organic phosphorus that escapes destruction in the water column is buried in refractory organic material or is regenerated and released into the interstitial water. Most of the interstitial-P diffuses out of the sediment into the overlying ocean. Some fraction of this interstitial phosphate is inorganically precipitated and subsequently trapped in an inorganic form (when this salt is a carbonate fluorapatite, we call it phosphorite; however, see McConnell, 1965). For this reason, an evaluation of the removal of phosphorus with organic carbon should include an estimate of the importance of its surrogate: phosphorite formation.

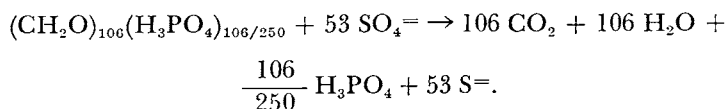
It is well known that several giant phosphorite deposits containing over 10^{16} moles-P exist in the geologic column (for example, the Permian Phosphoria Formation). These phosphate reservoirs each contain a mass of P larger than that dissolved in the present ocean ($\sim 3 \times 10^{15}$ moles). Thus each *could* have been formed by becoming the primary sink for the fluvial input to the oceans during several residence times of P in the oceans ($n \times 10^5$ yrs). The Phosphoria Formation is thought to have been deposited over about 6 m. y., requiring about 15 percent of the yearly fluvial P-flux. Thus giant deposits may have provided geochemically significant sinks for phosphorus from past oceans. They represent environments of deposition for which there is no modern analog, nor is there a generally-accepted model of their formation (Burnett and Sheldon, 1979; Bendor, 1980; Sheldon, 1981). Only recently have attempts been made to incorporate the episodicity of phosphogenesis (Cook and McElhinny, 1979) into our understanding of global paleoceanography (Arthur and Jenkyns, 1981; Piper and Codispotti, 1975).

It has long been accepted that the origin of phosphorite deposits is in some way associated with biological processes (Kazakov, 1938; Youseff, 1965; McConnell, 1965). Most nodular phosphorite deposits on continental margins appear to be relict (Kolodny and Kaplan, 1970), although occurrences beneath the highly productive southwest African and Peruvian coastal zones are forming today (Veeh, Calvert, and Price, 1974; Baturin, Merkulovo, and Chalou, 1972; Burnett, Veeh, and Soutar, 1980). The probable mode of formation of shallow-water deposits by alternate phosphatization and reworking during eustatic sealevel changes has been well described (Veeh, Calvert, and Price, 1974). However, it is unlikely that such shelf deposits are important in the removal of phosphorus from the recent ocean, since (1) most non-deltaic shelves are considered to be primarily areas of erosion or reworking, rather than depositional environments (Emery, 1968; van Andel and Curray, 1960), (2) the shelves were emergent during most of the recent (glacial) geologic past, and (3) the burial flux of P in these young deposits is trivial (Burnett, 1977).

Geosynclinal phosphorite deposits, however, form in deeper water beneath areas of productive upwelling in biogenic sediments along continental slopes and rises, particularly at the intersection of the oxygen-minimum zone with the bottom (D'Anglejan, 1968; Veeh, Burnett, and Soutar, 1973; Manheim, Rowe, and Jipa, 1975). Anoxic diagenesis of organic matter in the sediment column provides a source of dissolved phosphate in the interstitial water which promotes heterogeneous nucleation and growth of apatite over calcite and opal tests (Burnett, 1977). Thus some portion of the organic phosphorus delivered to the bottom is incorporated into the sediment as a diagenetic replacement product on biogenic detritus. If phosphorite burial is removing a significant proportion of the P-flux from today's ocean, it must be occurring here in continental rise sediments. Whether or not this dispersed phosphate deposition in rise sediments will ever become part of a future phosphorite formation is of course problematic but nevertheless is not germane to the flux argument we present below.

Organic phosphorus buried below the sediment surface faces three possible fates: (1) ultimate survival of regeneration with consequent burial as P_{org} , (2) regeneration to dissolved phosphate followed by release to the pore water with subsequent diffusion into the overlying water column (the fraction remaining in the pore water is quantitatively unimportant), and (3) regeneration to dissolved phosphate followed by precipitation as an authigenic phosphate salt to be buried ultimately as an inorganic surrogate for P_{org} . This last flux is what we wish to determine. Present sediment geochemical techniques cannot directly measure diagenetic phosphorite-P, because we are unable to separate this phase from the large burden of detrital apatite in hemipelagic sediments (Froelich, ms). We will estimate phosphorite burial indirectly as the difference between regenerated-P and diffusively-lost P in the same cores from areas of potential phosphorite formation. In the following discussion we use data from the continental slope and rise of western Africa in Hartmann

and others (1976) to calculate the P-regeneration flux and the diffusive-loss flux. We calculate extent of organic carbon regeneration from the sulfate reduction product sulfide, an index of the extent of organic matter oxidation (Berner, 1980; Goldhaber and Kaplan, 1980; Sweeney and Kaplan, 1980). We assume that authigenic phosphate minerals are formed only with phosphorus released during sulfate reduction (Burnett, 1977) according to the reaction



The reaction as written assumes that the P/C ratio in the organic matter undergoing diagenesis is equal to our average hemipelagic organic-P/organic-C ratio of 4×10^{-3} . We further assume that S^{2-} produced by this reaction is quantitatively sequestered into the solid phase by iron sulfide precipitation rather than lost by H_2S diffusion (as indicated by low H_2S concentrations found in hemipelagic areas with extensive sulfate reduction by Hartmann and others, 1976, and Froelich and others, 1979). According to these assumptions, the amount of P regenerated from a volume of sediment is given by the total sulfur content (minus a small amount of organically bound sulfur) $\times (1/53 \times 106/250)$. Calculated values of regenerated organic phosphorus from Hartmann's data are presented in table 4. These show that an insignificant proportion of the organic phosphorus originally present in these cores is regenerated by sulfate oxidation above 10 cm depth (that is, SO_4^{2-} reduction and S^{2-} entrapment are not important until below 10 cm). In core 12344 (at 700 m, the core nearest the O_2 -min), about 50 percent of the organic phosphorus has been regenerated below 100 cm. In other cores, the extent of regeneration deeper than 100 cm ranges from about 10 to about 35 percent. Extensive regeneration of organic phosphorus *may* be important in sediments near the oxygen minimum, but since these sediments account for only a small proportion of all hemipelagic sediments, we suggest that the average fraction of P_{org} regenerated within hemipelagic sediments (and thus the maximum potential phosphorite burial) is probably not more than about 25 percent of organic phosphorus burial.

What fraction of the regenerated phosphorus is actually trapped in marine sediments as phosphorite, and what fraction escapes by diffusion to the overlying seawater? We estimate upward diffusive fluxes of phosphate in the cores in table 4 and subtract that from estimated burial rates of regenerated-P in the same cores to obtain the phosphorite flux. To do this we have estimated dissolved phosphate gradients in those of Hartmann's cores in table 4 where interstitial phosphate data and sedimentation rate data are available (fig. 5). The results of these calculations (table 5) suggest that phosphate is not presently escaping from those deep sediments where significant regeneration has occurred (12310, 12392, 12379, 12347, and 12344). In fact, most of the diffusive loss of phosphate

TABLE 4
Estimates of extent of regeneration of organic phosphorus in
West Africa continental rise sediments (Hartmann and others, 1973)

Core no., Depth cm	Location and water depth		P_{org}	Fraction of P_{init} that is regenerated (= P_{reg}/P_{init})	
	S^{2-} umol g ⁻¹	P_{reg} umol g ⁻¹	umol g ⁻¹	P_{init} ***	
12344	15°25.7'N	17°20.5'W		613-748m	
0-8	<10	<0.1	5.4	5.5	<0.05
12-61	105	0.9	4.7	5.6	0.16
97-335	83	0.7	0.7	1.4	0.49
12327	23°07.9'N	17°44.1'W		2015-2115m	
0-35	<10	<0.1	4.9	5.0	<0.05
12379	23°08.4'N	17°44.7'W		2064-2151m	
0-20	<10	<0.1	3.9	4.0	<0.05
50-805	191	1.5	4.4	5.9	0.25
12392	25°10.3'N	16°50.7'W		2573-2610m	
0-50	<10	<0.1	3.5	3.6	<0.05
50-600	95	0.9	3.7	4.6	0.20
600-850	79	0.6	2.7	3.3	0.18
12347	15°49.5'N	17°50.7'W		2550-2747m	
0-13	10	0.1	2.9	3.0	<0.05
20-100	88	0.7	3.4	4.1	0.17
200-600	164	1.3	2.3	3.6	0.36

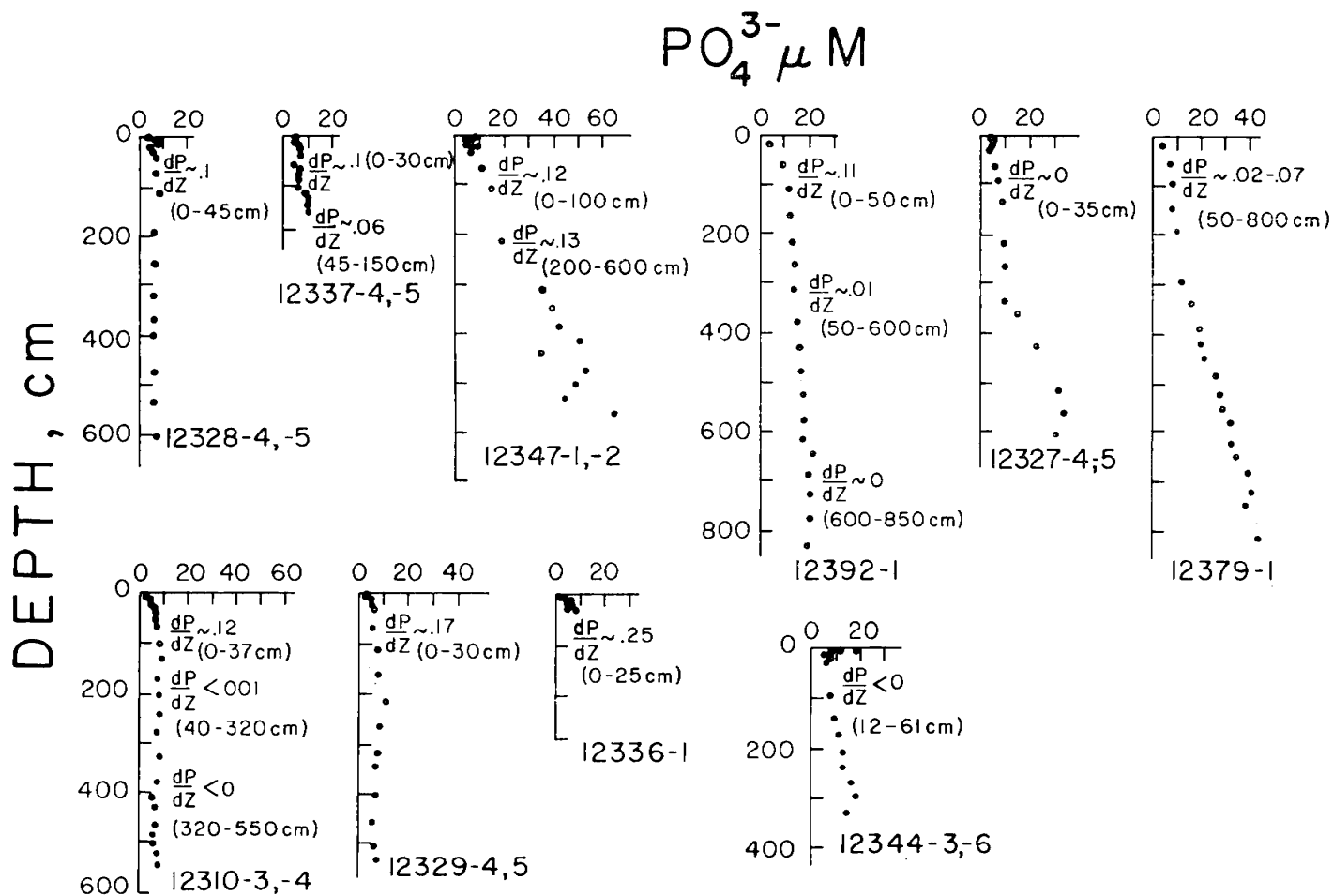
12328	21°08.7'N	18°34.4'W	2746-2822m	<0.05
0-20	<10		6.4	6.4
30-44	64		6.0	0.08
72-600	135		4.0	0.28
12337	15°58.4'N	18°07.1'W	3082-3095m	<0.05
0-30	<10		5.3	0.16
45-150	31		2.5	
12310	23°29.9'N	13°43.0'W	3069-3122m	<0.05
0-37	10		2.6	0.07
40-320	31		2.7	0.13
320-550	22		1.5	
12329	19°22.0'N	19°55.8'W	3314-3320m	<0.05
0-30	<10		3.0	
12336	16°14.3'N	20°25.5'W	3645-3670m	<0.05
0-25	<10		2.8	

$$* S^{2-} = \left[\Sigma S - \frac{C_{org}}{25} \right] \frac{1}{32}$$

$$** P_{reg} = S^{2-} \times \frac{1}{53} \times \frac{106}{250} \quad (\text{see text})$$

$$*** P_{init} = P_{reg} + P_{org}$$

Total sulfur (ΣS), organic carbon (C_{org}) and organic phosphorus (P_{org}) data are from Hartmann and others (1976). Station locations and water depths are from Seibold (1972).



is occurring from the uppermost sediment, evidently shallower than the present depth of onset of extensive sulfate diagenesis.

It is possible that the present dissolved phosphate profiles (and thus our estimate of diffusive P-loss) represent present conditions, whereas the regenerated organic phosphorus (as calculated from the sulfide burial) represents relict reactions that occurred at some past time, presumably when the sediment was at or near the surface. Since pore water profiles can adjust much more rapidly to changes in accumulation rates and reaction rates than can solid phases (Lasaga and Holland, 1976; Froelich and others, 1979), buried phases reflect "past" events, and pore water profiles represent "present" occurrences. If present conditions in the upper 50 cm of these cores are an indication of the conditions prevailing at the time when deeper sediments were being deposited and regenerated, then we would argue from the calculations in table 5 and phosphate pore water profiles in figure 5 that all the regenerated-P has escaped by diffusion except at one site: core 12344, at the depth of impingement of the O_2 -min with the bottom. If present conditions in the upper 50 cm of these sediments do not reflect past conditions (that is, if more regenerated-P was trapped), then the maximum fraction of the initial P_{org} that was trapped as phosphorite is about 25 percent (table 5, last column).

These arguments require a phosphorite burial flux less than or equal to 25 percent that of organic-phosphorus burial or about $\leq 1 \times 10^{-9}$ moles-P $cm^{-2}yr^{-1}$. It is unlikely that this value is too small, and the real value is very likely to be much nearer zero than our estimate. This is less than 10 percent of the input flux.

III. Burial of Phosphatic Fish Debris

Lowenstam (1974) has estimated that secretion of phosphatic fish debris is several orders of magnitude larger than the other potential phosphorus hard parts for which we have data. Thus we may concentrate exclusively on fish debris. Taking Ryther's (1969) world fish production estimate of 2.4×10^{13} g yr^{-1} (dry weight) and Hutchinson's (1952) estimate that the world's fish catch contains less than 1 percent by weight P (presumably mostly in hard parts), we estimate a maximum annual production of phosphatic fish debris of 2.1×10^{-9} moles-P $cm^{-2}yr^{-1}$. This value is at the low end of our estimated pre-man fluvial phosphorus flux (table 3). Thus phosphatic fish debris can be a significant sink only if all of the production is buried intact.

As Arrhenius (1963) has pointed out, fish debris appears to be dissolving in slowly accumulating pelagic sediments. Only fish teeth and shark denticles (very resistant) are recognized in pelagic sediments of all

← Fig. 5. Dissolved, interstitial phosphate versus depth plotted for those cores in table 4 where both interstitial phosphate and accumulation rate data are available. The gradients (dP/dz) were estimated as straight-line segments through the data in the depth interval indicated and are given in $nmoles\ cm^{-1}$. The upward diffusive fluxes calculated from these gradients are presented in table 5. Data are from Hartmann and others, 1976.

TABLE 5
Comparison of upward diffusive PO_4^{3-} flux and downward burial flux of regenerated-P

Core no.	Depth interval cm	Accumulation rate* $\text{g cm}^{-2} 10^{-3} \text{ yr}^{-1}$	$\text{P}_{\text{reg}}^{**}$ $\mu\text{mol g}^{-1}$	$\text{P}_{\text{reg}}^{**}$ Accumulation rate $\mu\text{mole-P cm}^{-2} 10^{-3} \text{ yr}^{-1}$	Upward PO_4^{3-} flux*** $\mu\text{mole-P cm}^{-2} 10^{-3} \text{ yr}^{-1}$	Phosphorite burial† $\mu\text{mole-P cm}^{-2} 10^{-3} \text{ yr}^{-1}$	Fraction†† %
12344	12-61	4.0	0.9	3.6	<0	3.6	16
12327	0-35	4.0	<0.1	<0.4	~0	0.4	5
12379	50-805	14.0	1.6	22.0	2-9	13-20	15-23
12392	0-50	2.8	<0.1	<.28	12.4	0	
"	50-600	6.0	0.9	5.4	1.1	4.3	16
"	600-850	3.0	0.5	1.5	~0	1.5	18
12347	20-100	6.7	0.8	5.4	13.5	0	0
"	200-605	18.0	1.3	23.0	14.6	8	13
12328	30-44	4.6	0.4	1.8	11.2	0	0
12337	0-30	5.3	<0.1	<.53	11.2	0	0
"	45-150	4.7	0.4	2.1	6.8	0	0
12310	0-37	1.7	<0.1	<.17	13.5	0	0
"	40-320	3.4	0.2	.68	<1.1	<0.4	4
"	320-550	2.2	0.2	.44	<0	0.44	13
12329	0-30	1.5	<0.1	<.15	19.0	0	0
12336	0-25	1.6	<0.1	<.16	28.0	0	0

* Bulk sediment accumulation rates derived from data in tables 2 and 3 of Hartmann and others (1976).

** Values from column 3 of table 4 for depth intervals shown.

*** Upward diffusive flux of PO_4^{3-} calculated from PO_4^{3-} gradients estimated in figure 5 and from apparent interstitial diffusion coefficient for PO_4^{3-} of $D_{\text{HPO}_4^{2-}}^* \sim 3.6 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ (Krom and Berner, 1980a).

† The phosphorite burial flux is given by the regenerated-P accumulation rate minus the upward flux.

†† Fraction of initial organic phosphorus that is transformed to phosphorite and buried as an inorganic surrogate.

ages (Helms and Reidel, 1971), so that extensive pelagic burial of fish debris is an unlikely phosphorus sink. P-accumulation rates measured on a strip sample of a giant piston core taken under the central gyre in the north Pacific (Hollister and others, ms; Doyle and Riedel, 1979) showed that P in the $> 20 \mu\text{m}$ fraction (mostly nodular fish bones, ootoliths, and vertebrae) accumulated at rates of only 0.06×10^{-9} moles-P $\text{cm}^{-2}\text{yr}^{-1}$ (Froelich, ms and 1979). Thus open ocean fish debris phosphorus burial is clearly not a significant sink.

However, Ryther (1969) has suggested that more than 99 percent of the world fish production occurs over continental shelves, narrow near-shore upwelling areas, and open ocean upwelling zones which together comprise only about 10 percent of the oceanic surface area and generally overlie rapidly accumulating hemipelagic sediments. Rapid sedimentation rates favor incorporation into the sediment before complete dissolution. If most fish debris is buried in hemipelagic sediments before dissolution, it could balance a small portion (< 20 percent) of the estimated river influx of phosphorus.

We present here two arguments that suggest that only a fraction of the fish debris produced in very productive areas is incorporated into the sediments. The first argument is based on comparing measured burial rates of fish debris with estimates of fish debris production in the same area. The second argument is based on comparing fish scale production and preservation.

The Callao Fishery, Peru.—DeVries (ms) has separated fish debris in several cores raised from the upper continental slope off Callao, Peru, one of the richest fisheries in the world (Ryther and others, 1971; Gulland, 1971) (table 6). Based on the average fish debris content (almost entirely anchoveta) in two of these cores that have been dated (DeMaster, ms), we estimate the burial flux of phosphorus in fish debris at these two sites to be less than 125 and 325×10^{-9} moles-P $\text{cm}^{-2}\text{yr}^{-1}$, respectively (table 7). (We ignore possible consequences of shifts in productivity, compaction, and sedimentation rate changes and simply take the "average" burial rate over the last several thousand years as probably lying in this range. We implicitly assume that productivity today is about the same as that during the time span represented by the sediment record.)

We estimate the fraction of the fish debris production that is buried in the Callao area by extrapolating production data for the entire Peruvian fishery (table 7). Pre-fishery fish production in the whole Peruvian fishery (which escapes predatory bird exportation) is estimated at 15 to 23×10^{12} g-wet fish yr^{-1} . This is equivalent to about 6.19×10^8 moles-P yr^{-1} in fish debris. Since about 15 percent of the Peruvian fish catch is in the Callao fishery, we prorate the production and deposition of fish debris accordingly and conclude that the production of phosphorus in fish debris in the Callao Zone is about 720 to 2160×10^{-9} moles-P $\text{cm}^{-2}\text{yr}^{-1}$ (table 7).

If cores W-7706-37 and -40 are typical of sediments in the Callao Zone accumulating fish debris, then the fraction of fish debris phosphorus preserved is about

$$\frac{< 125.325 \times 10^{-9} \text{ moles-P cm}^{-2}\text{yr}^{-1}}{720.2160 \times 10^{-9} \text{ moles-P cm}^{-2}\text{yr}^{-1}} \lesssim 6.45 \text{ percent}.$$

We can also compare production and burial rates of fish scales, an independent means of estimating the fraction of fish-P preserved. The net fish scale production in the Callao Zone is about 1 to 1.5 scales $\text{cm}^{-2}\text{yr}^{-1}$ (table 8). In core W 7706-40, scales accumulated at rates of about 0.10 $\text{cm}^{-2}\text{yr}^{-1}$ above 55 cm (fig. 6). Thus fish scale preservation is about 10 percent of the net production, in agreement with our estimate of total fish debris preservation in the Callao fishery. Similar estimates of fish scale preservation/production ratios for both sardine and anchovy off the southern California coast range from 10 to 20 percent, based on data for fish scale production and accumulation in the Santa Barbara and Soledad Basins, southern California (tables 9 and 10).

TABLE 6
Callao fish debris data

I. Percent fish debris (dry wt) in surface and sub-surface sediment on the upper continental slope off Peru. Average over the whole upper slope (core depths of 2 m) is about 0.2 percent (DeVries, ms).					
Core number	W7706-4	W7706-37	W7706-40	W7706-41	W7706-45
Water depth	325 m	370 m	186 m	411 m	810 m
Location	12°58.9'S 76°58.9'W	13°37.8'S 76°50.9'W	11°15.3'S 77°57.8'W	11°20.6'S 78°07.0'W	11°26.6'S 78°17.2'W
	Percent fish debris				
Surface (0-5 cm)	0.15	0.36	0.58	0.42	0.09
Subsurface (>5 cm)	—	0.26	0.23 0.19	0.25	—
II. Burial rates of fish debris-P					
	W7706-37	W7706-40			
1. Fish debris content of sediment below 5 cm	0.26%	0.21%		DeVries, ms	
2. Phosphorus content of fish debris	12%			Suess, unpub.	
3. Bulk dry density	~0.25 g cm^{-3}	~0.25 g cm^{-3}		Keller and Busch, 1978 DeMaster, ms	
4. Sedimentation rates of upper 20 cm. These rates are based on straight lines through log activity C-14 and Pb-210 versus depth plots, and thus are upper limits (see DeMaster, ms).	<0.05 cm yr^{-1}	<0.16 cm yr^{-1}		DeMaster, ms	
P-accumulation rates (upper limits):					
	<126 $\times 10^{-9}$ moles-P $\text{cm}^{-2}\text{yr}^{-1}$		<325 $\times 10^{-9}$ moles-P $\text{cm}^{-2}\text{yr}^{-1}$		

TABLE 7
Callao fish debris production estimate

<u>Pre-fishery fish-production in the whole Peruvian fishery</u>	18.0×10^{12} g wet fish yr^{-1} 20.0 25.0	Anonymous, 1974 Ryther, 1971 Gulland, 1971
Predatory bird exportation	— 2.5	Gulland, 1971
<u>Net Peruvian fish production</u>	$15 \text{ to } 23 \times 10^{12}$ g wet fish yr^{-1}	
Dry weight/wet weight	$\times 25\%$	Sanchez and Lam, 1970
% Fish debris-P (hard parts)	$\times 0.5\text{-}1.0\%$	Hutchinson, 1952; Bacigalupo and others, 1963
<u>Peruvian fish debris-P production</u>	$6 \text{ to } 9 \times 10^8$ moles-P yr^{-1}	
Callao fishery $\cong 15\%$ of Peru fishery		Borgo, Vasquez, and Paz, 1967, 1969 Vasquez, Paz, and Hidalgo, 1970
Area Callao fishery $\sim 1.25 \times 10^{14}$ cm^2		Borgo, Vasquez, and Paz, 1969 Sanchez, 1966
<u>Callao fish debris-P net deposition flux:</u>	$720\text{-}2160 \times 10^{-8}$ moles-P $\text{cm}^{-2}\text{yr}^{-1}$	

TABLE 8
Callao anchoveta fish scale production

Net Callao anchovy production 0.17-0.26 g cm ⁻² yr ⁻¹	(from information in table 8)
1 anchovy = 10 g	Simpson, Buzeta, and Gill, 1969
# scales/anchoveta = 600	DeVries, ms
Net Callao fish scale production: 1 to 1.5 scale cm ⁻² yr ⁻¹	

This information suggests that about 10 percent of the world fish debris phosphorus is preserved, while 90 percent is dissolved before burial. If 10 percent of the total production is buried, then the burial flux of phosphorus in fish debris is about 0.2×10^{-9} moles-P cm⁻²yr⁻¹. This value is much smaller than estimates both of the riverine P-input and of the P-removal rates by other processes. Thus phosphatic fish debris burial is probably not a significant P-sink.

IV. Phosphorus Burial With Biogenic Calcium Carbonates

We have summarized the available data for phosphorus concentrations of highly calcareous sediments (> 90 percent CaCO₃) in table 11. We will thus estimate the P-content of foraminiferal and coccolithiphorid tests from analyses of fossils in pelagic sediments and bypass the important question of whether the tests gain or lose P after the organisms die (Morse, 1974; deKanel and Morse, 1978). Literature values (entries 1-5 in table 11) would suggest that "average" biogenic calcite contains about 300 ± 80 ppm phosphorus. Forams and coccoliths likely contain different concentrations of phosphorus. Since the burial ratio of coccoliths to forams presumably varies from place to place in the ocean, the CaCO₃-P

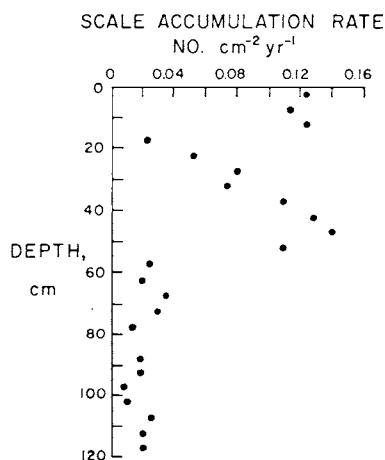


Fig. 6. Accumulation rates of all fish scales versus depth in core W7706-40. Rates are about 0.1 cm⁻²yr⁻¹ above 55 cm to about 0.02 scale cm⁻²yr⁻¹ below 55 cm. Bulk accumulation rates are from information in table 6 (DeMaster, ms; Keller and Busch, 1978). Fish scale data are from DeVries (ms).

TABLE 9
Santa Barbara anchovy fish scale production

<u>Pre-fishery southern California stock</u>	2.0×10^{12} g wet fish	Messersmith, 1969
Average age — 2 years	$\times 0.5$	
<u>Pre-fishery southern California production</u>	1.0×10^{12} g wet fish yr^{-1}	
Santa Barbara Basin fishery = 7% of southern California fishery	$\times 0.07$	Messersmith, 1969
<u>Santa Barbara fish production</u>	0.07×10^{12} g wet fish yr^{-1}	
1 anchovy = 20 g	$\times 0.05$	Messersmith, 1969
# scales/anchovy = 100	$\times 1000.$	Soutar and Isaacs, 1969
<u>Santa Barbara scale production</u>	3.5×10^{12} scales yr^{-1}	
<u>Net Santa Barbara scale production flux</u>	0.035 scales $\text{cm}^{-2}\text{yr}^{-1}$	Anonymous, 1951
<u>Santa Barbara scale accumulation rate</u>	0.004 scales $\text{cm}^{-2}\text{yr}^{-1}$	Soutar and Isaacs, 1969
<u>Scale preservation</u> = $\frac{0.004}{0.035} = 11\%$		

TABLE 10
Santa Barbara sardine scale production

<u>Pre-fishery southern California stock</u>	5.0×10^{12} g wet fish	
Average age = 3 years	$\times 0.33$	Felin and Phillips, 1948
<u>Pre-fishery southern California production</u>	1.65×10^{12} g wet fish yr^{-1}	
Santa Barbara Basin fishery = 4.5% of southern California fishery	$\times 0.045$	Sette, 1969
<u>Santa Barbara fish production</u>	0.075×10^{12} g wet fish yr^{-1}	
1 sardine = 100 g	$\times 0.01$	Felin and Phillips, 1948
# scales/sardine = 2400	$\times 2400.$	Soutar and Isaacs, 1969
<u>Santa Barbara scale production</u>	1.8×10^{12} scales yr^{-1}	
Santa Barbara area = 1.02×10^{14} cm^2		Anonymous, 1951
<u>Net Santa Barbara scale production flux</u>	0.018 scales $\text{cm}^{-2}\text{yr}^{-1}$	
<u>Santa Barbara scale accumulation rate</u>	0.0036 scales $\text{cm}^{-2}\text{yr}^{-1}$	Soutar and Isaacs, 1969
<u>Scale preservation</u> = $\frac{0.0036}{0.0180} = 20\%$		

TABLE 11
Phosphorus concentrations in highly calcareous sediments

1. Data from the Swedish Deep-Sea Expedition (Pettersson, 1952: v. V (2), VI (2))			
Sample no.	Sediment depth, cm	% CaCO ₃	ppm-P
74	25	96	260
	100	90	220
75	180	95	220
	460	93	220
	860	94	260
91	420	93	310
	600	100	175
2-61B-2-61	1015	98	220
2-61B-2-62	27	94	130
2. El Wakeel and Riley (1961)			
6 (Discovery "D")	—	91	310
3. Marchig (1972)			
SK 116	95	92	440
KK 125	120	91	390
KK 164	20	90	260
	30	93	420
	50	94	270
	90	97	340
	140	91	220
	180	94	270
KK 169		92	350
SK 170	10-40	93	460
4. Cook (1977)			
5A	2-4	90	344
5. Correns (1937) Calculated on basis of regression of % CaCO ₃ vs. % P ₂ O ₅ from equa- torial Atlantic Meteor Expedition (1925-1927)			
	—	100	350
6. Froelich (1979b)			
*RC-10-114 (bulk sample)	0-2	100	304
*RC-10-114: slightly sonicated			
<20 μ m (79% by weight)	0-2	100	365
>20 μ m (21% by weight)	0-2	100	100
*RC-10-114: severely sonicated			
<20 μ m (93% by weight)	0-2	100	320
>20 μ m (7% by weight)	0-2	100	60
7. Froelich (1979b)			
**G76-5-15GC1: severely sonicated	0-5	86	—
>150 μ m	0-5	100	40 \pm 3
**G76-5-15GC1: slightly sonicated	0-5	61-86	—
>150 μ m	(15 samples between 0-50 cm)	100	48 \pm 16

* RC-10-114: central equatorial Pacific, 2791 m deep (above CCD),
11°11'S 162°55'W.

Bulk analysis (INAA): 40.3 \pm 0.5% Ca (100.8 \pm 2.5% CaCO₃)
0.085 \pm 0.001% Al(<1% "clay")

** G76-5-15GC1: central equatorial Atlantic, 3685 m deep (above CCD), 0°02.1'S
14°58.4'W. This sample was 85% CaCO₃ and presumably contained
significant detrital clays. Thus no attempt was made to analyze the
fine fraction.

content of calcareous-rich sediments should vary accordingly. This effect may produce the rather large variations in phosphorus concentrations observed in calcareous-rich sediments (for example, table 11).

Froelich (ms) differentiated between foram-P and coccolith-P by size fractionation of pure calcareous oozes (table 11: 6 and 7). By maintaining both mass balances and phosphorus balances for each sample, and by observing that increasing severity of sonication during wet sieving has the combined effect of diluting the coccolith split ($< 20 \mu\text{m}$) with foram fragments while cleansing the foram splits (> 20 and $> 150 \mu\text{m}$) of coccoliths entrapped in unbroken foram chambers, he was able to separate crudely calcite-P into foram and coccolith fractions. These data suggest that the forams in both pelagic equatorial Atlantic and Pacific sediments are characterized by phosphorus concentrations of about 50 ppm. The phosphorus content of the coccolith fraction is less certain but apparently is about 400 ppm.

Taking foram-P as 50 ppm and coccolith-P as 400 ppm, the "average" biogenic calcite ($300 \pm 80 \text{ ppm-P}$) consists of 70 percent coccoliths and 30 percent forams. This agrees well with the work of Bishop and others (1977) and Honjo (1978) who found that coccoliths comprise over 65 percent of the vertical particulate flux of calcite, and with Broecker (1973) who found that 50 to 90 percent of the calcite in a wide variety of recent sediments is as coccoliths. However, Bramlette (1958) and Honjo (1976) have described calcareous sediments containing less than 50 percent coccoliths.

To calculate the burial flux of P in calcite, we will take the average calcite-P as 300 ppm, corresponding to a P/C mole ratio of 1×10^{-3} . Assuming that phosphorus is completely released to seawater upon calcite dissolution below the calcite compensation depth (Morse and Cook, 1978; however, see Correns, 1937 and Arrhenius, 1952), then, since the total carbon burial rate is $1.8 \times 10^{13} \text{ moles-C yr}^{-1}$ of which 80 percent is removed as CaCO_3 (see sec. I), burial of phosphorus in calcite is about $4 \times 10^{-9} \text{ moles-P cm}^{-2}\text{yr}^{-1}$. Thus calcite-P burial is as significant as organic-P burial ($4 \times 10^{-9} \text{ moles-P cm}^{-2}\text{yr}^{-1}$ or about 40 percent of input).

V. Inorganic Removal of Phosphorus

At least three inorganic processes could be important in removing phosphate from seawater (in addition to phosphorite formation, which we have discussed as a biologically-associated deposit): sorption onto detrital clays, precipitation of non-calcium-containing phosphate salts from pore waters, and removal both directly and indirectly during mid-ocean ridge hydrothermal processes. There can be no significant removal by low-temperature basalt-seawater exchange since the slightly negative interstitial phosphate gradients measured at the basalt/basal sediment interface are too small to allow a significant flux into the basalt (fig. 1: see discussion of low-temperature weathering input).

There is little quantitative information regarding the importance of clays sorbing or desorbing phosphate. Arrhenius (1952, p. 41 and 42 and references therein) and a few others have cited examples of apparent P-enrichment in some North Equatorial "pelagic clays". These observations are often cited as examples of P-sorption onto deep-sea clays, rendering red clays more phosphatic than shales or igneous rocks. A careful check of the original data in all cases has convinced us that these high phosphorus data (up to 0.6 percent-P in a few cases) are associated either with Tertiary clays or with volcanogenic deposits similar to those described by Berner (1973) and Froelich, Bender, and Heath (1977). Thus clays on the present seafloor are apparently not P-enriched. (The reason for enrichment in deep-sea clays, possibly during the Miocene period of extensive global phosphogenesis, is an interesting question!) We are not aware of any other data permitting quantification of a clay-sorbed P-flux to sediments. Since about 90 percent of the total (particulate plus dissolved "reactive") P-flux to the oceans is carried by particulates, these reactive-P fluxes will be difficult to decipher from solid phase data. They could be very important and remain a serious uncertainty in the phosphorus cycle.

Reduced iron phosphate (vivianite) and magnesium ammonium phosphate (struvite) are suspected of forming in reducing lake and estuarine sediments (Emerson and Widmer, 1978; Emerson, 1976; Martens, Berner, and Rosenfeld, 1978; Elderfield and others, 1981; Bray, Bricker, and Troup, 1973), but there is no evidence that burial of these phases is an important P-sink.

Berner (1973) has proposed the removal of seawater phosphate by scavenging onto fresh ferric oxyhydroxides produced during hydrothermal processes at actively spreading ridge crests (see, also, Correns, 1937; Revelle, 1944; Arrhenius, 1952). Hot hydrothermal seawater solutions debouching from vents near the ridge crest are laden with dissolved Fe^{2+} which oxidizes upon contact with oxygenated seawater and precipitates as ferric oxyhydroxides. These oxides scavenge phosphate plus a variety of other trace elements from seawater and settle to the sea floor to form metalliferous sediments containing up to 0.6 percent-P. Phosphorus accumulation rates measured in such sediments across the East Pacific Rise are two orders of magnitude higher than the oceanic average. Scaled to a global basis, metalliferous sedimentation could be responsible for removing from 1.1 to 1.6×10^{-9} moles-P $\text{cm}^{-2}\text{yr}^{-1}$ from the world's oceans (Froelich, Bender, and Heath, 1977). This estimate of metalliferous sedimentation is probably too high since hydrothermal processes on fast-spreading rise crests such as the East Pacific Rise may be exponential functions of spreading rate (Bostrom, 1973). We will thus adopt the lower end of this range as the most probable value: 1.1×10^{-9} moles-P $\text{cm}^{-2}\text{yr}^{-1}$.

Berner (1973) and Froelich, Bender, and Heath (1977) presented several indirect lines of evidence supporting a scavenged-from-seawater source for the phosphorus in metalliferous sediments rather than a source

associated with the hydrothermal solutions. The source of metalliferous-P could be decided unequivocally from a knowledge of the P-concentration of the hydrothermal vent solutions themselves (Corliss and others, 1979; Edmond and others, 1979a, b). Data from the cool vents of the Galápagos Ridge sampled during the Edmond, Corliss, and Gordon dives with D/V Alvin (Galápagos II: March 1979; data from Froelich, ms and 1979) suggest that P is depleted in hydrothermal emanations (fig. 7) and thus cannot be the source of metalliferous-P. Preliminary data from the hot vents at 21°N on the East Pacific Rise confirm this (Edmond, personal commun.). Thus Berner's (1973) conclusion that the phosphorus in metalliferous sediments derives from seawater appears sound, and our flux calculation is appropriate.

CONCLUSIONS

Our estimates of phosphorus burial fluxes and the marine P-cycle are summarized in table 12 and in a simple box model (fig. 8). Organic phosphorus and calcium carbonate-phosphorus make up about 40 percent each of the total identified removal, while phosphorite burial and hydrothermal-P comprise about 10 percent each. The sum of the estimated "reactive" phosphorus burial fluxes equals about 10×10^{-9} moles-P

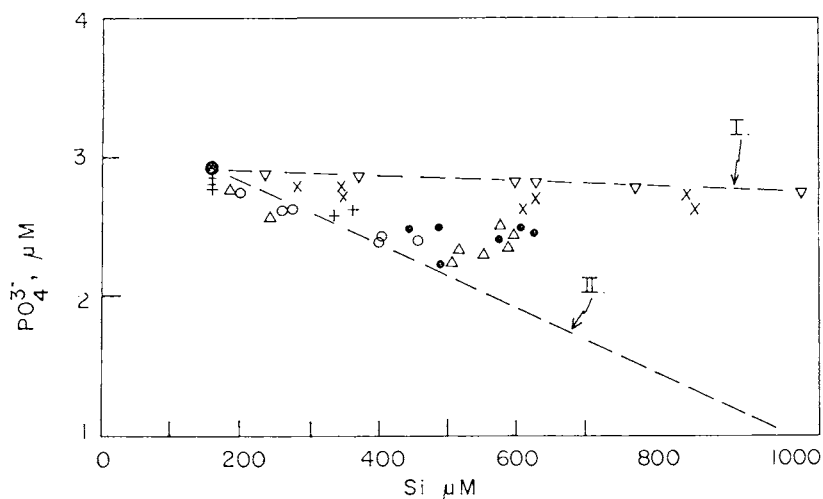


Fig. 7. Dissolved P and Si in Galapagos rift hydrothermal solutions collected by Edmonds, Corliss, and Gordon with the submersible D/V Alvin (Galapagos II; March, 1979). Si concentrations represent mixing between bottom water and high-temperature silica-enriched hydrothermal solutions (Corliss and others, 1979). Increasing silica concentrations on this plot are representative of increasing temperature and thus an increasing proportion of hydrothermal water in the sample. A decrease in phosphate with increasing Si suggests that the hydrothermal solutions are depleted in P relative to seawater. I: theoretical mixing line between bottom water phosphate (●) and a high-temperature hydrothermal solution (endmember) devoid of phosphate (that is, $\text{PO}_4 \approx 0$ at 380°C, or 24 mM-Si). II: theoretical mixing line between bottom water phosphate and a low-temperature solution devoid of phosphate (that is, $\text{PO}_4 = 0$ at 18°C, or 1 mM-Si). ○ Dive 898, X — 900, + — 900, ● — 902, Δ — 903, ▽ — 904.)

TABLE 12
Summary of P-burial fluxes

	10^{-9} moles $\text{cm}^{-2}\text{yr}^{-1}$
Organic phosphorus	4
Phosphorites	<1
$\text{CaCO}_3\text{-P}$	4
Hydrothermal	1.1
Fish debris	<0.2
TOTAL	10

$\text{cm}^{-2}\text{yr}^{-1}$, requiring a river water "reactive" P-concentration of about $1\ \mu\text{M}$. The residence time of P in the oceans is thus about 8×10^4 yrs.

No one sink is responsible for the majority of phosphate removal, although about 90 percent of the burial is associated with biogenic fluxes. The vast majority of deep-sea regenerated phosphate is released during organic carbon oxidation, and only a small portion derives from calcite dissolution below the CCD. If the oceans are to maintain a steady-state phosphorus cycle, then increased burial in one sink (for example, phosphorites) must be compensated by decreased burial in another sink or by enhanced input. It is not intuitively obvious how the mechanisms for such "sink-switching" might operate. It is clear, however, that the marine

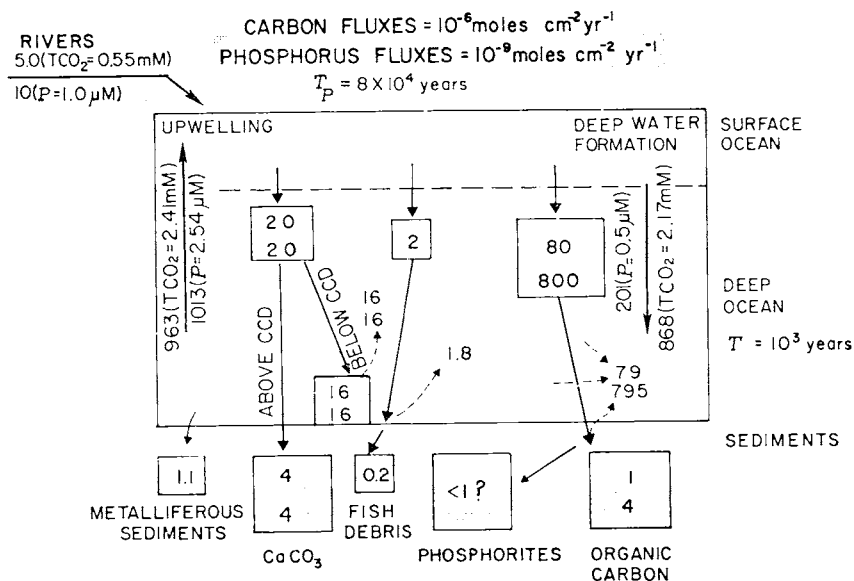


Fig. 8. Two-box model of the oceanic phosphorus and carbon cycles. Fluxes are in units of moles per cm^2 of ocean surface per yr. Appropriate phosphate and T-CO₂ concentrations of rivers and upwelling and deep-water sources are given in parentheses. Carbon model is based on Broecker (1981) and references therein.

phosphorus cycle is a complex system with no one simple control on the deep-sea phosphate concentration.

According to the model presented in figure 8, the required river water concentration is about $1 \mu\text{M-P}$, near the middle of our "reasonable" pre-agricultural dissolved phosphate river flux estimates (table 3). Thus steady-state arguments do not require the existence of significant unaccounted-for sinks. Neither, however, do these arguments eliminate the possibility of such undiscovered fluxes.

REFERENCES

- Altschuler, Z. S., 1973, The weathering of phosphate deposits—geochemical and environmental aspects, in Griffith, E. J., and others, eds., *Environmental Phosphorus Handbook*: New York, John Wiley & Sons, p. 33-96.
- D'Anglejan, B. F., 1968, Phosphate diagenesis of carbonate sediments as a mode of *in situ* formation of marine phosphorites: *Canadian Jour. Earth Sci.*, v. 5, p. 81-87.
- Anonymous, 1951, The commercial fish catch of California for the years 1948-1949 with yield per area of the California sardine fishing grounds, 1937-1959: California Dept. of Fish and Game, *Fish Bull.*, v. 80, 87 p.
- 1974, Report of the fourth session of the panel of experts on stock assessment of Peruvian Anchoveta: *Inst. del Mar del Peru Bull.*, v. 2 (10), p. 605-719.
- Arrhenius, G. O., 1952, Sediment cores from the East Pacific: Reports of the Swedish Deep-Sea Expedition 1947-1948, v. 5, p. 95-202.
- 1963, Pelagic sediments, in Hill, M. N., ed., *The Sea*, v. 3: New York, John Wiley & Sons, p. 655-727.
- Arthur, M. A., and Jenkyns, H. C., 1981, Phosphorites and paleoceanography, in Berger, W. H., ed., *Geology of Oceans Symposium: Internat. Geol. Cong.*, 26th, Paris 1980, *Proc. (Oceanol. Acta Spec. Pub.)*, p. 83-96.
- Atlas, E., ms, 1976, Phosphate equilibria in sea water and interstitial waters: Ph.D. thesis, Oregon State Univ., 154 p.
- Atlas, E., and Pytkowicz, R. M., 1977, Solubility behavior of apatite in seawater: *Limnology Oceanography*, v. 22, p. 290-300.
- Bacigalupo, A., Vidalon, C., Briceno, O., and Telley, J., 1963, Experiencias sobre el empleo de anchoveta fresco (*Engraulis ringens*) in la alimentacion de cerdos: *Anales cient.*, Univ. Agraria, La Molina, Peru, v. 1 (3), p. 291-318.
- Baturin, G. N., 1972, Phosphorus in interstitial waters of sediments of the southeastern Atlantic: *Oceanology*, v. 12, p. 849-855.
- 1978, Phosphorites: Moscow, Nauka., P. P. Shirshow Inst. Oceanology, Acad. Sci. USSR, 232 p. (in Russian).
- Baturin, G. N., Merkulov, K. I., and Chalou, P. I., 1972, Radiometric evidence for recent formation of phosphatic nodules in marine shelf sediments: *Marine Geology*, v. 13, p. M37-M41.
- Bender, M., Broecker, W., Gornitz, V., Middel, U., Kay, R., Sun, S. S., and Biscaye, P., 1971, Geochemistry of three cores from the East Pacific Rise: *Earth Planetary Sci. Letters*, v. 12, p. 425.
- Bentor, Y. K., 1980, Marine Phosphorites—Geochemistry, Occurrence, Genesis: *Soc. Econ. Paleontologists and Mineralogists Spec. Pub.* 29, 249 p.
- Berner, R. A., 1973, Phosphate removal from sea-water by absorption on volcanogenic ferric oxides: *Earth Planetary Sci. Letters*, v. 18, p. 77-86.
- 1980, *Early Diagenesis: A Theoretical Approach*: Princeton, N.J., Princeton Univ. Press, 241 p.
- Bishop, J. K., Collier, R. W., Ketten, D. R., and Edmond, J. M., 1980, The chemistry, biology, and vertical flux of particulate matter from the upper 1500m of the Panama Basin: *Deep-Sea Research*, v. 27A, p. 615-640.
- Bishop, J. K., Edmond, J. M., Ketten, D. R., Bacon, M. P., and Silker, W. B., 1977, The chemistry, biology and vertical flux of particulate matter from the upper 100m of the equatorial Atlantic Ocean: *Deep-Sea Research*, v. 24, p. 211-548.
- Bloch, S., 1978, Phosphorus distribution in smectite-bearing basal metalliferous sediments: *Chem. Geology*, v. 22, p. 353-359.
- Borgo, J. L., Vasquez, I., and Paz, A., 1967, La Pesqueria Maritima Peruana durante 1966: *Inst. del Mar del Peru, Informe* 19, 118 p.
- 1969, La Pesqueria Maritima Peruana durante 1967: *Inst. del Mar del Peru, Informe* 26, 46 p.

- Bostrom, K., 1973, The origin and fate of ferromanganese active ridge sediments: Stockholm Contr. Geology, v. 27, p. 149-243.
- Bramlette, M. N., 1958, Significance of coccolithophorids in calcium carbonate deposition: Geol. Soc. America Bull., v. 69, p. 121-126.
- Bray, J. T., Bricker, O. P., and Troup, B. N., 1973, Phosphate in interstitial waters of anoxic sediments: Oxidation effects during sampling procedure: Science, v. 180, p. 1362-1364.
- Broecker, W. S., 1971a, A kinetic model for the chemical composition of sea-water: Quaternary Research, v. 1, p. 188-207.
- 1971b, Calcite accumulation rates and glacial to interglacial changes in oceanic mixing, in Turekian, K. K., ed., The Late Cenozoic Glacial Ages: New Haven, Yale Univ. Press, p. 239-265.
- 1973, Factors controlling CO₂ content in the oceans and atmosphere, in Woodwell, G. M., and E. V. Pecan, eds., Carbon and the Biosphere: Washington, D.C., U.S. Atomic Energy Comm., p. 32-50.
- 1974, Chemical Oceanography: New York, Harcourt Brace Jovanovich, Inc., 214 p.
- 1981, Glacial to interglacial changes in ocean chemistry, in Kraus, E., ed., Co-operative Inst. Marine and Atmospheric Studies Symposium volume: Univ. of Miami (in press).
- Brooks, R. R., Presley, B. J., and Kaplan, I. R., 1968, Trace elements in the interstitial waters of marine sediments: Geochim. et Cosmochim. Acta, v. 32, p. 397-414.
- Burnett, W. C., 1977, Geochemistry and origin of phosphorite deposits from off Peru and Chile: Geol. Soc. America Bull., v. 88, p. 813-823.
- Burnett, W. C., and Sheldon, R. P., 1979, Report on the Marine Phosphatic Sediments Workshop: Honolulu, East-West Center Pub., 65 p.
- Burnett, W. C., Veeh, H. H., and Soutar, A., 1980, U-series, oceanographic and sedimentary evidence in support of recent formation of phosphate nodules off Peru, in Bentor, Y. K., ed., Marine Phosphorites: Soc. Econ. Paleontologists and Mineralogists Spec. Pub. 29, p. 61-71.
- Butler, E. I., and Tibbits, S., 1972, Chemical Survey of the Tamar Estuary: Marine Biol. Assoc. United Kingdom Jour., v. 52, p. 681-699.
- Clarke, F. W., 1924, The data of geochemistry, 5th ed.: U.S. Geol. Survey Bull., v. 770, p. 518-1358.
- Cook, N. W., ms, 1977, A preliminary investigation of the distribution of phosphorus in North Atlantic Ocean deep-sea and continental slope sediments: M.S. thesis, Florida State Univ., Tallahassee.
- Cook, P. J., 1974, Geochemistry and diagenesis of interstitial fluids and associated calcareous oozes: Deep-Sea Drilling Project Leg 27, Site 262, Timor Trough: Washington, D.C., Govt. Printing Office, v. 27, p. 463-480.
- Cook, P. J., and McElhinny, M. W., 1979, A re-evaluation of the spatial and temporal distribution of sedimentary phosphate deposits in the light of plate tectonics: Econ. Geology, v. 74, p. 315-330.
- Copin-Montegut, C., and Copin-Montegut, G., 1972, Chemical analysis of suspended particulate matter collected in the northeast Atlantic: Deep-Sea Research, v. 19, p. 445-452.
- 1978, The chemistry of particulate matter from the south Indian and Antarctic Oceans: Deep-Sea Research, v. 25, p. 911-931.
- Corliss, J. B., Dymond, J., Gordon, L. I., Edmond, J. M., vonHerzen, R. P., Ballard, R. D., Green, K., Williams, D., Bainbridge, A., Crane, K., and van Andel, T. H., 1979, Submarine thermal springs on the Galapagos Rift: Science, v. 203, p. 1073-1083.
- Correns, C. W., 1937, Die Sedimente des Aequatorialen Atlantischen Ozeans: Wiss. Ergebnisse der Deutschen Atlantischen Expedition auf dem Forsch. und Vermessungsschiff "Meteor" 1925-1927, v. III (3), 298 p.
- Deevey, E. S., 1973, Sulfur, nitrogen and carbon in the biosphere, in Woodwell, G. M., and Pecan, E. V., eds., Carbon and the Biosphere: U.S. Atomic Energy Comm., p. 182-190.
- deKanel, J., and Morse, J. W., 1978, The chemistry of orthophosphate uptake from sea-water onto calcite and aragonite: Geochim. et Cosmochim. Acta, v. 42, p. 1335-1340.
- DeMaster, D. J., ms, 1979, The marine budgets of silicon and silicon-32: Ph.D. thesis, Yale Univ., 308 p.
- DeVries, T. J., ms, 1979, Nekton remains, diatoms, and Holocene upwelling off Peru: M.S. thesis, Oregon State Univ., Corvallis, Oregon, 85 p.

- Doyle, P. S., and Riedel, W. R., 1979, Cretaceous to Neogene ichthyoliths in a giant piston core from the central North Pacific: *Micropaleontology*, v. 25, p. 337-364.
- Edmond, J. M., Measures, C., McDuff, E. R., Chan, J. H., Grant, G., Gordon, L. I., and Corliss, J. B., 1979a, Ridgecrest hydrothermal activity and the balances of the major and minor elements in the ocean: the Galápagos data: *Earth Planetary Sci. Letters*, v. 46, p. 1-19.
- Edmond, J. M., Measures, C., Mangum, B., Grant, B., Slater, F. R., Collier, R., Hudson, A., Gordon, L. I., and Corliss, J. B., 1979b, On the formation of metal-rich deposits at ridge crests: *Earth Planetary Sci. Letters*, v. 46, p. 19-31.
- El Wakel, S. K., and Riley, J. P., 1961, Chemical and mineralogical studies of deep-sea sediments: *Geochim. et Cosmochim. Acta*, v. 25, p. 110-146.
- Elderfield, H., Luedtke, N., McCaffrey, R. J., and Bender, M., 1981, Benthic flux studies in Narragansett Bay: *Am. Jour. Sci.*, v. 281, p. 768-787.
- Emerson, S., 1976, Early diagenesis in anaerobic lake sediments: Chemical equilibrium in interstitial waters: *Geochim. et Cosmochim. Acta*, v. 40, p. 925-934.
- Emerson, S., Jahnke, R., Bender, M., Froelich, P., Klinkhammer, G., Bowser, C., and Setlock, G., 1980, Early diagenesis in sediments from the Eastern Equatorial Pacific, I. Pore water nutrient and carbonate results: *Earth Planetary Sci. Letters*, v. 49, p. 57-80.
- Emerson, S., and Widmer, G., 1978, Early diagenesis in anaerobic lake sediments — II. Thermodynamics and kinetic factors controlling the formation of iron phosphate: *Geochim. et Cosmochim. Acta*, v. 42, p. 1307-1316.
- Emery, K. O., 1968, Relict sediments on continental shelves of the world: *Am. Assoc. Petroleum Geologists Bull.*, v. 52, p. 445-464.
- Emigh, G. D., 1973, Economic phosphate deposits, in Griffith, E. J., *et al.*, eds., *Environmental Phosphorus Handbook*: New York, Wiley-Interscience, p. 97-116.
- Fellin, F. E., and Phillips, J. B., 1948, Age and length composition of the sardine catch off the Pacific coast of the United States and Canada, 1941-42 through 1946-47: *California Dept. Fish and Game Fisheries Bull.*, v. 69.
- Filipeck, L. H., and Owen, R. H., 1981, Diagenetic controls of phosphorus in outer shelf sediments from the Gulf of Mexico: *Chem. Geology*, v. 33, p. 181-204.
- Fleming, R. H., 1940, The composition of plankton and units for reporting population and production: *Pacific Sci. Cong.*, 6th, California, 1939, *Proc.*, v. 3, p. 535-540.
- Froelich, P. N., 1979, Analysis of organic carbon in marine sediments: *Limnology Oceanography*, v. 25, p. 524-572.
- , 1979, Marine Phosphorus Geochemistry: Ph.D. dissert., Univ. Rhode Island, 291 p.
- Froelich, P. N., Bender, M. L., and Heath, G. R., 1977, Phosphorus accumulation rates in metalliferous sediments on the East Pacific Rise: *Earth and Planetary Sci. Letters*, v. 34, p. 351-359.
- Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V., 1979, Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis: *Geochim. et Cosmochim. Acta*, v. 43, p. 1075-1090.
- Garrels, R. M., MacKenzie, F. T., and Hunt, C., 1975, Chemical cycles and the global environment: Los Altos, Calif., William Kaufmann, Inc., 206 p.
- Garrels, R. M., and MacKenzie, F. T., 1971, *Evolution of Sedimentary Rocks*: New York, Newton, 397 p.
- Garrels, R. M., and Perry, E. A., 1974, Cycling of carbon, sulfur, and oxygen through geologic time, in Goldberg, M. N., ed., *The Sea*, v. 5: New York, Interscience, p. 303-336.
- Gibbs, R. J., 1972, Water Chemistry of the Amazon River: *Geochim. et Cosmochim. Acta*, v. 36, p. 1061-1066.
- , 1967, The geochemistry of the Amazon River system: I. The factors that control the salinity and the composition and concentration of the suspended solids: *Geol. Soc. America Bull.*, v. 78, p. 1204-1232.
- Gieskes, J. M., 1973, Interstitial water studies, Leg. 15: Alkalinity, pH, Mg, Ca, Si, PO₄, and NH₄: *Initial Repts. Deep-Sea Drilling Project*, v. 20, p. 813-829.
- Goldberg, E. D., Gross, G., Broecker, W. S., and Turekian, K. K., 1971, Radioactivity in the Marine Environment: Washington, D.C., Natl. Acad. Sci., p. 148.
- Goldhaber, M. B., and Kaplan, I. R., 1980, Mechanisms of sulfur incorporation and isotope fractionation during early diagenesis in sediments of the Gulf of California: *Marine Chemistry*, v. 9, p. 97-146.

- Graham, W. F., and Duce, R. A., 1979, Atmospheric pathways of the phosphorus cycle: *Geochim. et Cosmochim. Acta*, v. 43, p. 1195-1208.
- Gregor, B., 1970, Denudation of the continents: London, *Nature*, v. 228, p. 273-275.
- Gulbrandsen, R. A., and Roberson, C. E., 1973, Inorganic phosphorus in seawater, in Griffith, E. J. and others, eds., *Environmental Phosphorus Handbook*: New York, John Wiley & Sons, p. 117-140.
- Gulland, J. A., 1971, The fish resources of the ocean: Surrey, England, Food and Agricultural Organization, Fishing News, Ltd., 255 p.
- Hart, R., 1970, Chemical exchange between sea-water and deep ocean basalts: *Earth Planetary Sci Letters*, v. 9, p. 269-279.
- Hartmann, M., Müller, P. J., Suess, E., and van der Weijden, C. H., 1973, Oxidation of organic matter in recent marine sediments: "Meteor"-Forsch.-Ergebnisse, v. C(12), p. 74-86.
- 1976, Chemistry of Late Quaternary sediments and their interstitial waters from the NW African continental margin: "Meteor"-Forsch.-Ergebnisse, v. C(24), p. 1-67.
- Heath, R. T., Moore, T. C., and Dauphin, J. P., 1977, Organic carbon in deep-sea sediments, in Anderson, N. R., and Malahoff, A., eds., *The Fate of Fossil Fuel CO₂ in the Oceans*: New York, Plenum Press, p. 605-625.
- Helms, P. B., and Riedel, W. R., 1971, Skeletal debris of fishes: Initial Repts. Deep-Sea Drilling Project, v. 7, p. 1709-1720.
- Holeman, J. N., 1968, The sediment yield of major rivers of the world: *Water Resources Research*, v. 4, p. 737-747.
- Holland, H. D., 1972, Ocean water, nutrients, and atmospheric oxygen, in Ingerson, E., ed., *Proceedings International Conference of Hydrogeochemistry and Biogeochemistry*, Tokyo, 1970: Washington, D.C., Clarke Co.
- Hollister, C. D., Corliss, B. H., vonHerzen, B., Richardson, M. J., Dow, W., Heath, G. R., Prince, R., Epstein, G. B., Leinen, M., Doyle, P., Riedel, W., McDuff, R., Silva, A., Calnan, D., Baldwin, K., Hayes, D. E., and Tucholke, B. E., ms, 1978, A paleo-environmental model for Cenozoic sedimentation in the central north Pacific: Albuquerque, manuscript prepared for Sandia Workshop, Deep-Sea Disposal Program, Washington, D.C. Dept Energy.
- Honjo, S., 1976, Cocoliths: production, transportation and sedimentation: *Marine Micropaleontology*, v. 1, p. 65-79.
- 1978, Sedimentation of materials in the Sargasso Sea at 5,367m deep station: *Jour. Marine Research*, v. 36, p. 469-492.
- Hutchinson, G. E., 1951, The biochemistry of phosphorus, in Wolterink, L. J., ed., *The Biology of Phosphorus*: East Lansing, Michigan State College Press, p. 1-35.
- Jahnke, R. A., ms, 1981, Current phosphorite formation and the solubility of synthetic carbonate fluorapatite: Ph.D. dissert., Univ. Washington, 210 p.
- Judson, S., 1968, Erosion of the land: *Am. Scientist*, v. 56, p. 356-374.
- Kazakov, A., 1938, Phosphorite facies and the genesis of natural phosphates: *Soviet Geology*, v. 8, p. 33-47.
- Keller, G. H., and Busch, W. H., 1978, Patterns and processes of continental margin sedimentation off Peru — geotechnical properties and and sediment stability: *Geol. Soc. America Abs. with Program*, v. 10, no. 7, p. 433.
- Ketchum, B. H., Corwin, N., and Yentsch, C. S., ms, 1967, in *Biological, chemical and radiochemical studies of marine plankton*: Woods Hole Ocean. Inst. Blue Cover Rept. 67-27, p. 21-25.
- Knauer, G. A., Martin, J. H., and Bruland, K. W., 1979, Fluxes of particulate carbon, nitrogen and phosphorus in the upper water column of the northeast Pacific: *Deep-Sea Research*, v. 26 (1A), p. 97-108.
- Kolodny, Y., and Kaplan, I. R., 1970, Uranium isotopes in sea-floor phosphorites: *Geochim. et Cosmochim. Acta*, v. 35, p. 3-24.
- Koritnig, S., 1970, Phosphorus, in Wedepohl, K. H., ed., *Handbook of Geochemistry II 2, (15-F)*: Berlin, Springer-Verlag, p. 7-8.
- Krom, M. D., and Berner, R. A., 1980a, The diffusion coefficients of sulfate, ammonium and phosphate ions in anoxic marine sediments: *Limnology Oceanography*, v. 25, p. 327-338.
- 1980b, Adsorption of phosphate in anoxic marine sediments: *Limnology Oceanography*, v. 25, p. 797-806.
- 1981, The diagenesis of phosphorus in nearshore marine sediment: *Geochim. et Cosmochim. Acta*, v. 45, p. 207-216.

- Lasaga, A. C., and Holland, H. D., 1976, Mathematical aspects of non-steady state diagenesis: *Geochim. et Cosmochim. Acta*, v. 40, p. 257-266.
- Lemasson, L., Cremoux, J. L., and Montel, Y., 1977, Analyse des rapports C/N/P du seston dans la partie orientale de l'Atlantique equatorial: *Marine Chemistry*, v. 5, p. 171-181.
- Lerman, A., MacKenzie, F. T., and Garrels, R. M., 1975, Modeling of geochemical cycles: Phosphorus as an example: *Geol. Soc. America Mem.* 142, p. 205-218.
- Li, Yuan-Hui, 1972, Geochemical mass balance among lithosphere, hydrosphere and atmosphere: *Am. Jour. Sci.*, v. 272, p. 119-137.
- Liss, P. S., 1976, Conservative and non-conservative behavior of dissolved constituents during estuarine mixing, in Burton, J. D., and Liss, P. S., eds., *Estuarine Chemistry*: New York, Academic Press, p. 93-130.
- Livingstone, D. A., 1963, Chemical composition of rivers and lakes, in *Data of Geochemistry*: U.S. Geol. Survey Prof. Paper 440-D, p. 64.
- Lowenstam, H. A., 1974, Impact of life on chemical and physical processes, in Hill, M. N., ed., *The Sea*, v. 5: New York, John Wiley & Sons, p. 715-795.
- Mannheim, F., Rowe, G. T., and Jipa, D., 1975, Marine phosphorite formation off Peru: *Jour. Sed. Petrology*, v. 45, p. 243-251.
- McConnell, D., 1965, Precipitation of phosphates in sea-water: *Econ. Geology*, v. 60, p. 1054-1062.
- , 1973, *Apatite*: New York, Springer-Verlag, p. 111.
- McKelvey, V. E., 1973, Abundance and distribution of phosphorus in the lithosphere, in Griffith, E. J., and others, eds., *Environmental Phosphorus Handbook*: New York, John Wiley & Sons, p. 13-31.
- Marchig, V., 1972, Zur geochemie rezenter sedimente des Indischen Ozeans: "Meteor"-Forschungs-Ergebnisse, v. C(11), p. 1-104.
- Martens, C. S., Berner, R. A., and Rosenfeld, J. K., 1978, Interstitial water chemistry of anoxic Long Island Sound sediments. 2. Nutrient regeneration and phosphate removal: *Limnology Oceanography*, v. 23(4), p. 605-617.
- Martin, J. M., and Meybeck, N., 1979, Elemental mass-balance of material carried by major world rivers: *Marine Chemistry*, v. 7, p. 173-206.
- Messersmith, J. D., 1969, The northern anchovy (*Engraulis mordax*) and its fishery, 1965-1968: California Dept. Fish and Game, *Fish Bull.*, v. 147, 102 p.
- Morse, J. W., 1974, Dissolution kinetics of CaCO_3 in sea-water. V. Effects of natural inhibitors and the position of the chemical lysocline: *Am. Jour. Sci.*, v. 274, p. 638-647.
- Morse, J. W., and Cook, N., 1978, The distribution and form of phosphorus in North Atlantic Ocean deep-sea and continental slope sediments: *Limnology Oceanography*, v. 23, p. 825-830.
- Müller, P. J., and Suess, E., 1979, Productivity, sedimentation rate and sedimentary organic matter in the oceans — I. Organic carbon preservation: *Deep-Sea Research*, v. 26A, p. 1347-1362.
- Parker, R. L., 1967, Composition of the earth's crust, in Fleischer, M., ed., *Data of Geochemistry*: U.S. Geol. Survey Prof. Paper 440-D, p. 17.
- Parker, P. L., Behrens, E. W., Calder, J. A., and Schultz, D., 1972, Stable carbon isotope ratio variations in the organic carbon from Gulf of Mexico sediments: *Marine Sci.*, v. 16, p. 139-147.
- Pettersson, H., 1952, Reports of the Swedish Deep-Sea Expedition 1947-1948: Göteborg, Elanders Boktryckeri Artieborg.
- Piper, D. Z., and Codispotti, L. A., 1975, Marine phosphorite deposits and the nitrogen cycle: *Science*, v. 188, p. 15-18.
- Pomeroy, O. R., Smith, E. E., and Grant, C. M., 1965, The exchange of phosphate between estuarine water and sediments: *Limnology Oceanography*, v. 10, p. 167-172.
- Pytkowicz, R. M., and Kester, D. R., 1967, Relative calcium phosphate saturation in two regions of the north Pacific Ocean: *Limnology Oceanography*, v. 12, p. 714-718.
- Redfield, A. C., 1958, The biological control of chemical factors in the environment: *Am. Scientist*, v. 46, p. 205-222.
- Redfield, A. C., Ketchum, B. H., and Richards, F. A., 1963, The influence of organisms on the composition of sea-water, in Hill, M. N., ed., *The Sea*, v. 2: New York, John Wiley & Sons, p. 26-87.
- Revelle, R., 1944, Marine bottom samples collected in the Pacific Ocean by the Carnegie on its seventh cruise: Carnegie Inst. Washington Pub. 556.

- Riggs, S. R., 1980, Tectonic model of phosphate diagenesis, in Sheldon, R. P., and Burnett, W. C., eds., *Fertilizer mineral potential in Asia and the Pacific*: Honolulu, Hawaii, East-West Resources Systems Inst., p. 159-190.
- Riley, J. P., and Chester, R., 1971, *Introduction to Marine Chemistry*: New York, Academic Press, 465 p.
- Rittenberg, S. C., Emery, K. O., and Orr, W. L., 1955, Regeneration of nutrients in sediments of marine basins: *Deep-Sea Research*, v. 3, p. 23-45.
- Ronov, A. B., and Korzina, G. A., 1960, Phosphorus in sedimentary rocks: *Geochemistry*, v. 8, p. 805-829.
- Ronov, A. B., and Yaroshevsky, A. A., 1969, Chemical composition of the earth's crust, in Hart, P. M., ed., *The Earth's Crust and Upper Mantle*: Am. Geophys. Union. *Geophys. Mon.* 13, p. 37-57.
- Ryther, J. H., 1969, Photosynthesis and fish production in the sea: *Science*, v. 166, p. 72-76.
- Ryther, J. H., Menzel, D. W., Hurlbert, E. M., Lorenzen, C. J., and Corwin, N., 1971, The production and utilization of organic matter in the Peru coastal current: *Inv. Pesquera*, v. 35, p. 43-60.
- Sanchez, J. E., 1966, General aspects of the biology and ecology of the anchovy (*Engraulis ringens*): *Gulf and Caribbean Fish Institute Proc.*, v. 18, p. 84-93.
- Sanchez, J., and Lam, R., 1970, Algunas características físicas y sus rendimientos en productos pesqueros, en el Peru: *Inst. del Mar del Peru, Informe* 33, p. 92.
- Seibold, D., 1972, Cruise 25=1971 of the R/V METEOR: continental margin off West Africa: General report and preliminary results: *Meteor. Forsch. Ergebnisse*, v. C(10), p. 17-38.
- Sette, O. E., 1969, A perspective of a multispecies fishery: *California Cooperative Oceanic Fisheries Inv. Repts.*, v. 13, p. 81-87.
- Sheldon, R. P., 1981, Ancient marine phosphorites: *Ann. Rev. Earth Planetary Sci.*, v. 9, p. 251-284.
- Sholkovitz, E., 1973, Interstitial water chemistry of Santa Barbara Basin sediments: *Geochim. et Cosmochim. Acta*, v. 37, p. 2043-2073.
- Silker, W. B., 1964, Variations in elemental concentrations in the Columbia River: *Limnology Oceanography*, v. 9, p. 540-545.
- Sillén, L. G., 1967, The ocean as a chemical system: *Science*, v. 156, p. 1189-1197.
- Simpson, J. G., Buzeta, R., and Gil, E., 1969, Relacion longitudpeso de la anchoveta *Engraulis ringens* durante 1966: *Inst. fomento Pesquero, Chile Pub.*, v. 44, p. 26.
- Soutar, A., and Isaacs, J. D., 1969, History of fish populations inferred from fish scales in anaerobic sediments off California: *California Cooperative Oceanic Fisheries Inv. Repts.*, v. 13, p. 63-70.
- , 1974, Abundance of pelagic fish during the 19th and 20th centuries as recorded in anaerobic sediments off the Californias: *Fish Bull.*, v. 72, p. 257-274.
- Stefansson, U., and Richards, J. A., 1963, Processes contributing to the nutrient distributions off the Columbia River and Strait of Juan de Fuca: *Limnology Oceanography*, v. 8, p. 394-410.
- Stumm, W., 1973, The acceleration of the hydrogeochemical cycling of phosphorus, in Jenkins, S. H., and Ives, K. J., eds., *Phosphorus in freshwater and the marine environment*: New York, Pergamon, p. 131-144.
- Suess, Erwin, 1981, Phosphate regeneration from sediments of the Peru continental margin by dissolution of fish debris: *Geochim. et Cosmochim. Acta*, v. 45, p. 577-588.
- Suess, Erwin, and Müller, P. J., 1980, Productivity, sedimentation rate and sedimentary organic matter in the Oceans II — Elemental Fractionation: *Colloques. Inter. du Centre Natl. Recherche Sci.* No 293 — *Biogéochimie de la matière organique à L'interface eau-sédiment marin*, p. 17-26.
- Sweeney, R. E., and Kaplan, I. R., 1980, Diagenetic sulfate reduction in marine sediments: *Marine Chemistry*, v. 9, p. 165-174.
- Toth, D. J., and Lerman, A., 1977, Organic matter reactivity and sedimentation rates in the ocean: *Am. Jour. Sci.*, v. 277, p. 465-485.
- van Andel, T. H., and Curray, J. R., 1960, Regional aspects of modern sedimentation in northern Gulf of Mexico and similar basins and paleogeographic significance, in *Recent Sediments, Northwest Gulf of Mexico*: Tulsa, Okla., Am. Assoc. Petroleum Geologists, p. 345-364.
- Vasquez, I., Paz, A., and Hidalgo, R., 1970, La Pesqueria marítima Peruana durante 1969: *Inst. del Mar del Peru, Informe* 32, p. 85.

- Veeh, H. H., Burnett, W. C., and Soutar, A., 1973, Contemporary phosphorites on the continental margin of Peru: *Science*, v. 181, p. 844-845.
- Veeh, H. H., Calvert, S. E., and Price, N. B., 1974, Accumulation of uranium in sediments and phosphorites on the southwest African shelf: *Marine Chemistry*, v. 2, p. 189-202.
- Walker, J. C. G., 1974, Stability of atmospheric oxygen: *Am. Jour. Sci.*, v. 274, p. 193-214.
- Wedepohl, K. H., 1971, *Geochemistry*: New York, Holt, Rinehart and Winston, Inc., 216 p.
- Weimar, W., ms, 1973, Inositol phosphate esters in lake sediments: Ph.D. dissert., Univ. Wisconsin.
- White, R. H., and Miller, S. L., 1976, Inositol isomers: Occurrence in marine sediments: *Science*, v. 193, p. 885-886.
- Williams, P. M., 1968, Organic and inorganic constituents of the Amazon River: *Nature*, v. 218, p. 937-938.
- Youssef, M. I., 1965, Genesis of bedded phosphates: *Econ. Geology*, v. 60, p. 590-600.