

The Global Phosphorus Cycle

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INTRODUCTION

Phosphorus (P) is a limiting nutrient for terrestrial biological productivity that commonly plays a key role in net carbon uptake in terrestrial ecosystems (Tiessen et al. 1984, Roberts et al. 1985, Lajtha and Schlesinger 1988). Unlike nitrogen (another limiting nutrient but one with an abundant atmospheric pool), the availability of “new” P in ecosystems is restricted by the rate of release of this element during soil weathering. Because of the limitations of P availability, P is generally recycled to various extents in ecosystems depending on climate, soil type, and ecosystem level. The release of P from apatite dissolution is a key control on ecosystem productivity (Cole et al. 1977, Tiessen et al. 1984, Roberts et al. 1985, Crews et al. 1995, Vitousek et al. 1997, Schlesinger et al. 1998), which in turn is critical to terrestrial carbon balances (e.g., Kump and Alley 1994, Adams 1995). Furthermore, the weathering of P from the terrestrial system and transport by rivers is the only appreciable source of P to the oceans. On longer time scales, this supply of P also limits the total amount of primary production in the ocean (Holland 1978, Broecker 1982, Smith 1984, Filippelli and Delaney 1994). Thus, understanding the controls on P weathering from land and transport to the ocean is important for models of global change. In this paper, I will present an overview of the natural (pre-human) and modern (syn-human) global P mass balances, followed by in-depth examinations of several current areas of research in P cycling, including climatic controls on ecosystem dynamics and soil development, the control of oxygen on coupled P and Carbon (C) cycling in continental margins, and the role that P plays in controlling ocean productivity on Cenozoic timescales.

GLOBAL PHOSPHORUS CYCLING

Natural (pre-human) phosphorus cycle

The human impact on the global P cycle has been substantial over the last 150 years and will continue to dominate the natural cycle of P on the globe for the foreseeable future. Because this anthropogenic modification began well before scientific efforts to quantify the cycle of P, we can only guess at the “pre-anthropogenic” mass balance of P. Several aspects of the pre-anthropogenic sources and sinks of P are relatively well constrained (Fig. 1). The initial source of P to the global system is via the weathering of P during soil development, whereby P is released mainly from apatite minerals and made soluble and bioavailable (this process will be discussed at considerable length later). In contrast to this process of chemical weathering, the physical weathering and erosion of material from continents results in P that is typically unavailable to biota. An exception to this, however, is the role that physical weathering plays in producing fine materials with extremely high surface area/mass ratios. Phosphorus and other components may be rapidly weathered if this fine material is deposited in continental environments (i.e., floodplains and delta systems) where it undergoes subsequent chemical weathering and/or soil development. Thus, the total amount of P weathered from continents may be very different from the amount of potentially bioavailable P.

Apatite minerals, the dominate weathering source of P, vary widely in chemistry and

structure and can form in igneous, metamorphic, sedimentary, and biogenic environments. All apatite minerals contain phosphate oxyanions linked by Ca^{2+} cations to form a hexagonal framework, but they differ in elemental composition at the corners of the hexagonal cell (Table 1; McClellan and Lehr 1969, Hughes and Rakovan, this volume). By far the most abundant of the igneous apatite minerals, fluorapatite, is an early-formed accessory mineral that appears as tiny euhedral crystals associated with ferromagnesian minerals (McConnell 1973).

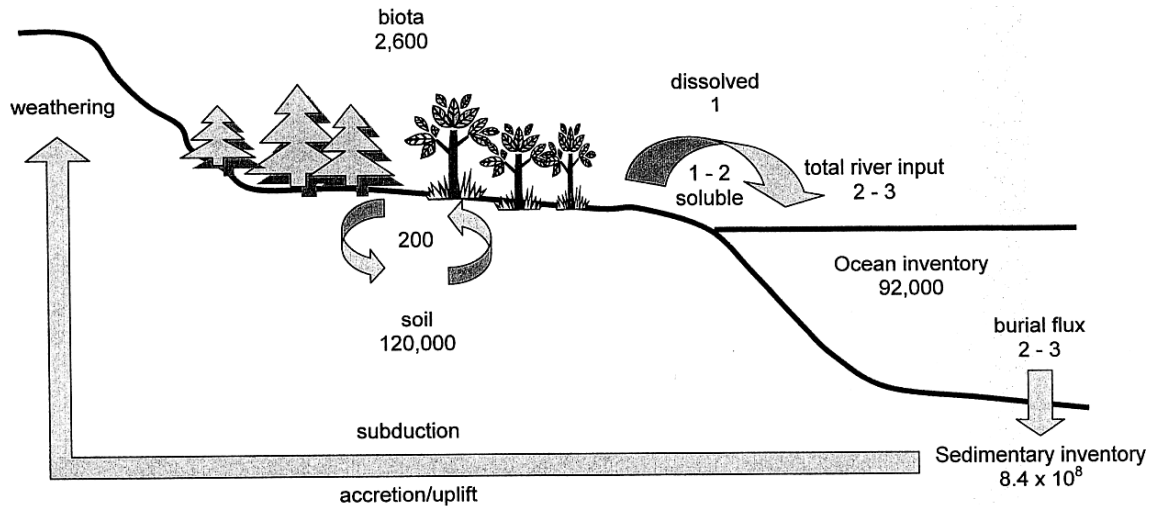


Figure 1. The natural (pre-human) dissolved phosphorus cycle, showing reservoirs (in Tg P) and fluxes (denoted by arrows, in Tg P/yr) in the P mass balance.

Table 1. Terminology and crystal chemistry of apatites.

<i>Mineral name</i>	<i>Chemical composition</i>
Fluorapatite (FAP)	$\text{Ca}_5 (\text{PO}_4)_3\text{F}$
Hydroxylapatite (HAP)	$\text{Ca}_5 (\text{PO}_4)_3\text{OH}$
Chlorapatite	$\text{Ca}_5 (\text{PO}_4)_3\text{Cl}$
Dahllite	$\text{Ca}_5 (\text{PO}_4, \text{CO}_3\text{OH})_3(\text{OH})$
Franconite (CFAP)	$\text{Ca}_5 (\text{PO}_4, \text{CO}_3\text{OH})_3(\text{F})$

After Phillips and Griffen (1981).

Apatite dissolution: phosphate rock and synthetic hydroxyapatite (HAP). The dissolution rate of apatite minerals has been the focus of a variety of relatively disparate studies. For example, the importance of P as a fertilizer and as an integral component of teeth and bone material has led to a wide range of P dissolution and retention studies. Most of the agricultural studies have focused on the dissolution of fertilizers, in which P has already been leached from phosphate rock ore (usually a mixed lithology of marine sediments containing high percentages of carbonate fluorapatite (CFAP), $\text{Ca}_5 (\text{PO}_4, \text{CO}_3\text{OH})_3(\text{F})$, as described in Filippelli and Delaney 1992a) and re-precipitated as a highly soluble phosphoric salts. Some studies, however, have investigated the dissolution of phosphate rock in laboratory experiments (Smith et al. 1974, 1977; Olsen 1975, Chien

et al. 1980, Onken and Matheson 1982). The medical studies have investigated the dissolution behavior of synthetic HAP (similar in composition to dahllite) in acidic solutions, especially to understand the processes of bone resorption and formation, as well as the formation of dental caries (cavities) (Christoffersen et al. 1978, Christoffersen 1981, Christoffersen and Christoffersen 1985, Fox et al. 1978, Nancollas et al. 1987, Constantz et al. 1995).

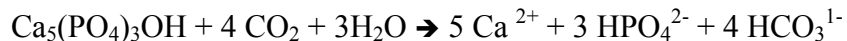
Several workers have attempted to develop dissolution rate equations to model apatite dissolution (Olsen 1975, Smith et al. 1977, Christoffersen et al. 1978, Fox et al. 1978, Chien et al. 1980, Onken and Metheson 1982, Hull and Lerman 1985, Hull and Hull 1987, Chin and Nancollas 1991). Rate equations from these models include zero order, first order, parabolic diffusion, mixed order, and other forms. The most current model (Hull and Hull 1987) focuses on surface dissolution geometry, which the authors argue fit the experimental results better than previous dissolution models. These experiments and the dissolution rate equations derived from them are missing the experimental conditions that replicate the natural dissolution processes and agents in soils, as they do not include the range of apatite mineralogies likely to be naturally weathering in soils.

Apatite dissolution: marine sediments and CFAP. Perhaps the most comprehensive and geologically appropriate laboratory examination of apatite dissolution has been performed on CFAP (francolite). Researchers focused on the marine P cycle have performed several studies on CFAP dissolution (Lane and Mackenzie 1990, 1991; Tribble et al. 1995), as well as CFAP precipitation in laboratory settings (Jahnke 1984, Van Cappellen and Berner 1988, Van Cappellen 1991, Filippelli and Delaney 1992b, 1993). These studies have focused on CFAP because of its importance as an authigenic marine mineral phase in terms of the oceanic P cycle (Ruttenberg 1993, Filippelli and Delaney 1996). Several general observations about apatite dissolution/ precipitation have been made. For example, the presence of Mg has been determined to retard CFAP formation (Atlas and Pytkowicz 1977), but the presence of other trace elements (e.g., Fe and Mn) appears to have little effect (Filippelli and Delaney 1992b, 1993).

In a study of the pH-dependence of CFAP dissolution, Lane and Mackenzie (1990, 1991) used a fluidized bed reactor to determine dissolution chemistry. As presented in Tribble et al. (1995), a Ca and fluorine (F)-depleted surface layer appears to form during early dissolution, followed by a later stage when stoichiometric dissolution is achieved. The incongruent initial dissolution is probably due to the removal of most or all of the F and some Ca in the depleted surface layer, and the formation of a hydrogen-calcium phosphate phase, which has also been observed by other workers (Atlas and Pytkowicz 1977, Smith et al. 1974, Driessens and Verbeeck 1981, Thirioux et al. 1990). This surface controlled reaction eventually achieves a steady state—the depleted surface layer does not change in depth and the solid effectively dissolves congruently (Tribble et al. 1995). Ruttenberg (1990, 1992) performed extensive dissolution experiments on fluorapatite (FAP), HAP, and CFAP, with a goal of developing an extraction scheme for the characterization of these mineral phases in marine sediments. Although geared toward extraction technique development, these studies showed increased dissolution rate with decreasing grain sizes, and higher dissolution rates of HAP and CFAP than FAP with moderately acidic pH values.

Phosphorus cycling in soils. The cycling of P in soils (see Fig. 1) has received much attention, both in terms of fertilization and the natural development of ecosystems. Of the approximately 122,600 Tg P within the soil/biota system on the continents, nearly 98% is held in soils in a variety of forms. The exchange of P between biota and soils is relatively rapid, with an average residence time of 13 years, whereas the average residence time of

P in soils is 600 years (Fig. 1). As noted above, the only significant weathering source for phosphorus in soils is apatite minerals. These minerals can be congruently weathered as a result of reaction with dissolved carbon dioxide:



In soils, P is released from mineral grains by several processes. First, the reduced pH produced from respiration-related CO₂ in the vicinity of both degrading organic matter and root hairs dissolves P-bearing minerals (mainly apatites) and releases P to root pore spaces (e.g., Schlesinger 1997). Second, organic acids released by plant roots also can dissolve apatite minerals and release P to soil pore spaces (Jurinak et al. 1986). Phosphorus is very immobile in most soils, and its slow rate of diffusion from dissolved form in pore spaces strongly limits its supply to rootlet surfaces (Robinson 1986). Furthermore, much of the available P in soils is in organic matter, which is not directly accessible for plant nutrition. Plants have developed two specific tactics to increase the supply of P to roots. First, plants and soil microbes secrete phosphatase, an enzyme that can release bio-available inorganic P from organic matter (McGill and Cole 1981, Malcolm 1983, Kroehler and Linkins 1988, Tarafdar and Claasen 1988). Second, the symbiotic fungi *mycorrhizae* can coat plant rootlets, excreting phosphatase and organic acids to release P and providing an active uptake site for the rapid diffusion of P from soil pore spaces to the root surface (Antibus et al. 1981, Bolan et al. 1984, Dodd et al. 1987). In exchange, the plant provides carbohydrates to the *mycorrhizal* fungi (Schlesinger 1997).

Phosphorus in soils is present in a variety of forms, and the distribution of P between these forms changes dramatically with time and soil development. The forms of soil P can be grouped into refractory (not readily bio-available) and labile (readily bio-available). The refractory forms include P in apatite minerals and P co-precipitated with and/or adsorbed onto iron and manganese oxyhydroxides (termed “occluded” P). The reducible oxyhydroxides have large binding capacities for phosphate, due to their immense surface area and numerous delocalized positively charged sites (e.g., Froelich 1988, Smeck 1985). The labile forms include P in soil pore spaces (as dissolved phosphate ion) and adsorbed onto soil particle surfaces (these forms are termed “non-occluded” P), as well as P incorporated in soil organic matter. On a newly exposed lithic surface, nearly all of the P is present as P in apatite. With time and soil development, however, P is increasingly released from this form and incorporated in the others (Fig. 2). Over time, the total amount of P available in the soil profile decreases, as soil P is lost through surface and subsurface runoff. Eventually, the soil reaches a terminal steady state, when soil P is heavily recycled and any P lost through runoff is slowly replaced by new P weathered from apatites at the base of the soil column.

Riverine transport of particulate and dissolved phosphorus. The eventual erosion of soil material and transport by rivers delivers P to the oceans. Riverine P occurs in two main forms: particulate and dissolved. Most of the P contained in the particulate load of rivers is held within mineral lattices and never participates in the active biogenic cycle of P. This will also be its fate once it is delivered to the oceans, because dissolution rates in the high pH and heavily buffered waters of the sea are exceedingly low. Thus, much of the net P physically eroded from continents is delivered relatively unaltered to the oceans, where it is sedimented on continental margins and in the deep sea, until subduction or accretion eventually returns P to be exposed on land again. Some of the particulate P is adsorbed onto soil surfaces, held within soil oxide, and incorporated into particulate organic matter. This P likely interacts with the biotic P cycle on land, and its fate upon transfer to the ocean is poorly understood. For example, P adsorbed onto soil surfaces may be effectively displaced by the high ionic strength of ocean water, providing an

additional source of P into the ocean. Furthermore, a small amount of the P incorporated into terrestrial organic matter may be released in certain environments during bacterial oxidation after sediment burial. Finally, some sedimentary environments along continental margins are suboxic or even anoxic, conditions favorable for oxide dissolution and release of the incorporated P.

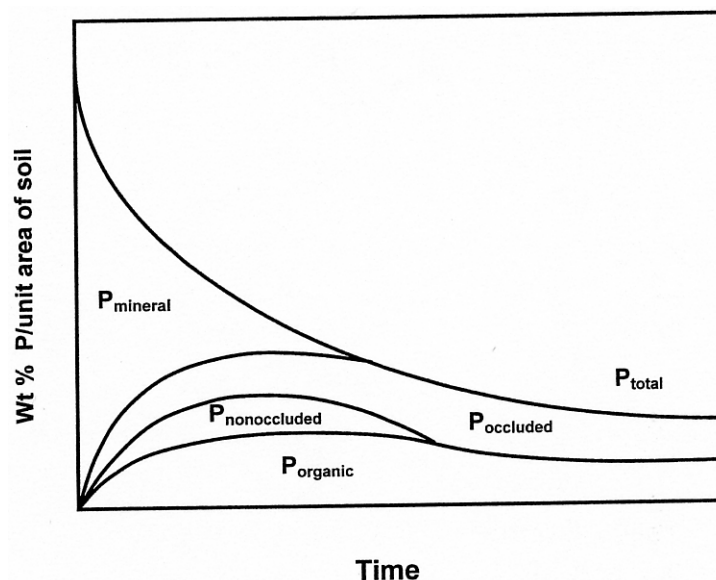


Figure 2. Modeled changes in soil phosphorus geochemistry over time (based on Walker and Syers 1976), showing transformation of mineral phosphorus into non-occluded and organic forms before eventual dominance of occluded (oxide-bound) and organic forms. The relative bio-reactivity of phosphorus increases from mineral to occluded to organic forms of phosphorus. Note the continual loss of total phosphorus from the system. From Filippelli and Souch (1999).

Several important studies have examined the transfer of P between terrestrial and marine environments (e.g., Froelich 1988, Berner and Rao 1994, Ruttenberg and Goñi 1997), but more work clearly needs to be done to quantify the interactions between dissolved and particulate P forms and the aquatic/marine interface. The net pre-human flux of dissolved P to the oceans is ~ 1 Tg P/year, with an additional 1-2 Tg P/year of potentially soluble P, bringing the total to about 2-3 Tg P/year. Thus, the residence time of biologically available P on land is about 40-60 kyr with respect to export to the oceans. It may be no coincidence that this residence time is of a glacial timescale—later I discuss the control of climate on the terrestrial P cycle. But clearly, the interaction between biologically available P on land and loss of this P to the oceans is relatively dynamic and speaks to the relatively rapid cycling of P on land.

Marine sedimentation. Once in the marine system, dissolved P acts as the critical long-term nutrient limiting biological productivity. Phosphate concentrations are near zero in most surface waters, as this element is taken up by phytoplankton as a vital component of their photosystems (phosphate forms the base for ATP and ADP, required for photosynthetic energy transfer) and their cells (cell walls are comprised of phospholipids). Dissolved P has a nutrient profile in the ocean, with a surface depletion and a deep enrichment. Furthermore, deep phosphate concentrations increase with the age of deep water, and thus values in young deep waters of the Atlantic are typically $\sim 1.5 \mu\text{M}$ whereas those in the older Pacific are $\sim 2.5 \mu\text{M}$ (Broecker and Peng 1982). Once incorporated into plant material, P roughly follows the organic matter loop, undergoing active recycling in the water column and at the sediment/water interface.

Phosphorus input and output are driven to steady state mass balance in the ocean by biological productivity. As mentioned previously, one of the difficulties with accurately determining the pre-anthropogenic residence time of P in the ocean is that input has been nearly doubled due to anthropogenic activities, and thus we must resort to estimating the burial output of P, a technique plagued by site-to-site variability in deposition rates and poor age control. Estimates of P burial rates have been performed by a variety of methods, including determination via P sedimentary sinks (e.g., Froelich et al. 1982, 1983) and riverine suspended matter fluxes calibrated to the P geochemistry of those fluxes (Ruttenberg 1993). We have used an areal approach to quantifying the modern P mass balance (Table 2; Filippelli and Delaney 1996). Using this areal approach, we find that the output term for the P mass balance might be higher than previously estimated, and therefore the P residence time might be shorter than previously thought (Table 2).

Table 2. Phosphorus accumulation, burial, and the modern oceanic phosphorus mass balance (from Filippelli and Delaney 1996).

	<i>Equat. Pacific^a</i>	<i>All mod/high prod. pelagic^b</i>	<i>Low prod. pelagic regions^c</i>	<i>Cont. margins^d</i>	<i>Whole Ocean^e (1993)</i>	<i>Previous estimates Ruttenberg et al. (1982)^f Froelich</i>	
P acc. rate ($\mu\text{mol cm}^{-2} \text{ kyr}^{-1}$)	19	28	10	500	--	--	--
Area (10^6 km^2)	30	276	60	25	361	--	--
P burial rate ^g (10^{10} mol P/yr)	0.6	7.7	0.6	12.5	21.0	8.0–18.5	5.0
P residence time (kyr) ^h					15	16–38	60

^a Mean of all samples from 0 to 1 Ma in Filippelli and Delaney (1996).

^b Defined as a region with a primary productivity greater than $35 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Berger and Wefer 1991). Phosphorus accumulation rate is a mean of various moderate to high productivity pelagic regions (e.g., Southern Ocean, equatorial Atlantic, equatorial Pacific; compiled by Filippelli 1997a).

^c Defined as a region with a primary productivity less than $35 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Berger and Wefer 1991). Phosphorus accumulation rate is a mean of various low productivity pelagic regions (e.g., pelagic red clay provinces; compiled by Filippelli 1997a).

^d Defined as area above 200-m water depth (Menard and Smith 1966). Phosphorus accumulation rate is the low range value of various continental margin regions (e.g., upwelling and non-upwelling environments; compiled by Filippelli 1997a). The low range was used because many of the published phosphorus concentration values included non-reactive phosphorus components, which do not interact with the dissolved marine phosphorus cycle.

^e Filippelli and Delaney (1996). Whole ocean is sum of all moderate to high productivity pelagic regions, low productivity pelagic regions, and continental margins.

^f As revised in Froelich (1984).

^g Phosphorus accumulation rate multiplied by area.

^h Calculated as whole ocean phosphorus inventory ($3.1 \times 10^{15} \text{ mol P}$) divided by whole ocean phosphorus burial rate ($21 \times 10^{10} \text{ mol P/yr}$).

Averaging across regions with varying P accumulation rates undoubtedly imparts a relative error of at least 50% to the burial rate value derived here. Also, some restricted environments exhibit quite high but spatially variable P burial rates (e.g., phosphatic continental margin environments, Froelich et al. 1982; hydrothermal iron sediments, Froelich et al. 1977, Wheat et al. 1996). The areal approach is a more direct route to quantifying the burial terms in the P mass balance, and indicates that reactive P burial in continental margin sediments accounts for about 60% of the oceanic output, with deep sea sediments nearly equivalent as a sink.

Although the areal approach is a promising and direct method for quantifying the modern P mass balance and potentially determining past variations in the balance, we are still greatly limited by the sparse data that presently exist for P geochemistry and accumulation rates, especially along continental margins. Interestingly, the concentration of reactive P in sediments displays a relatively narrow range in both deep-ocean and continental margin environments (Filippelli 1997a). The major force driving variations in accumulation rates from site to site is the sedimentation rate, termed the ‘master variable’ in P accumulation by Krajewski et al. (1995) (Fig. 3). Thus, the P accumulation rate at any given site is most responsive to sedimentation rate—this also results in reactive P burial rates being approximately equally distributed between continental margin and deep ocean regions, even though continental margins represent only a fraction of the total ocean area (Filippelli and Delaney 1996, Compton et al. 2000).

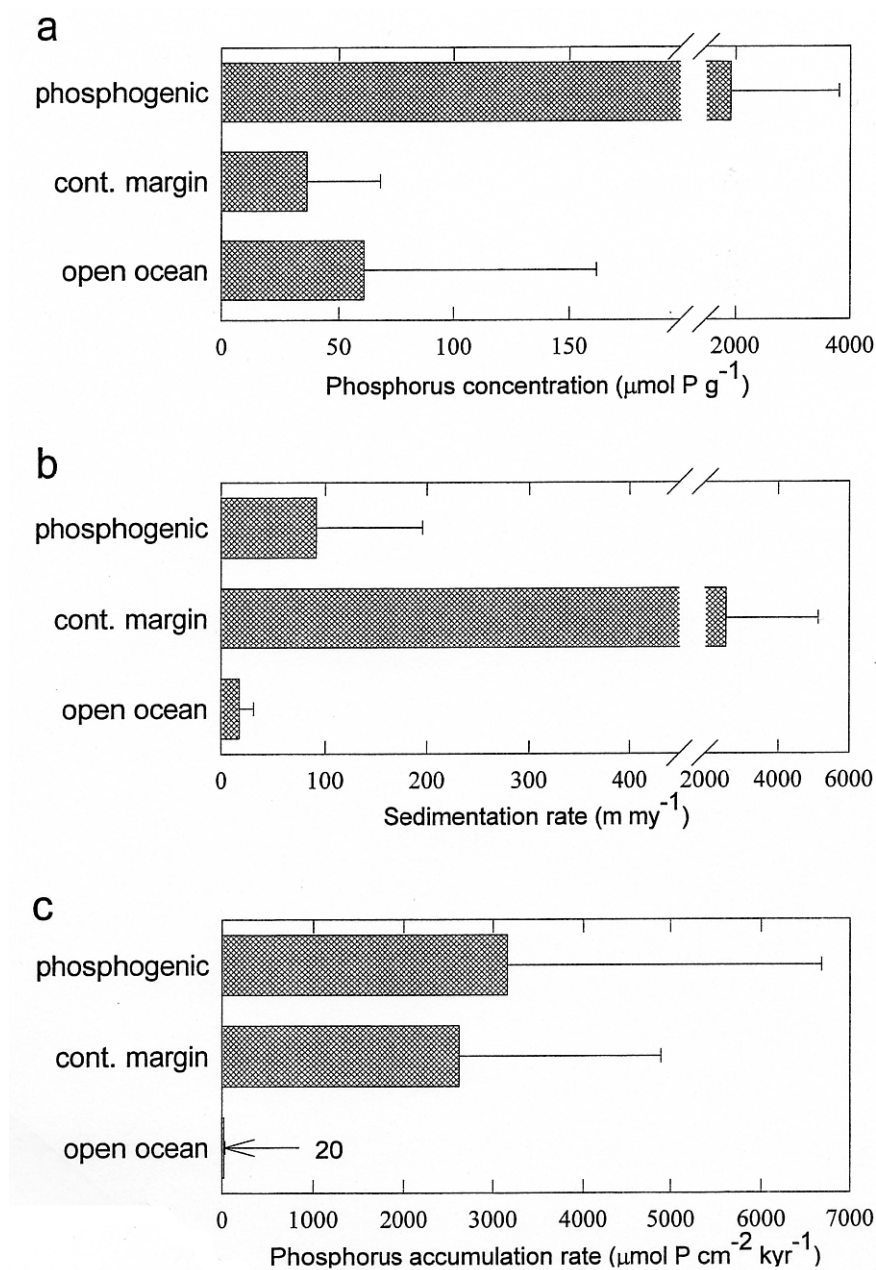


Figure 3. Plots of (a) phosphorus concentration, (b) sedimentation rate, and (c) phosphorus accumulation rate for open ocean, continental margin, and phosphogenic environments.

Modern phosphorus cycle

Human impacts have been manifested for decades at least in a variety of settings. Since the awareness that P is an important plant nutrient, the application of P directly to fields to increase crop yields has increasingly dominated the P cycle. The early source of this fertilizer P was from rock phosphate, generally phosphate-rich sedimentary rocks (phosphorites) mined in the 19th century from a variety of settings in Europe and the US. This P-rich rock was ground and applied to fields, where it significantly enhanced crop yield after initial application. Farmers soon found, however, that crop production significantly decreased after several years of application of this rock fertilizer. Unbeknownst to the farmers, the P-rich rock they were applying to their fields was also rich in cadmium and uranium, both naturally found in the organic-rich marine sediments that are precursors to phosphorite rocks but also toxic to plants (Schlesinger 1997). Many previously productive fields became barren due to this practice, and the awareness of the heavy-metal enriched P fertilizers led to the development of a variety of leaching techniques to separate the beneficial P from the toxic heavy metals. The perfection of this technique and the co-application of P with nitrogen (N), potassium (K), and other micronutrients in commercially available fertilizers boomed during the “Green Revolution,” the period after WW II that saw prosperity in some countries and exponential growth in global populations. The irony of the moniker “Green Revolution” has become apparent, as the production of enormous amounts of food fueled by fertilizers to feed a growing global population has caused a variety of detrimental environmental conditions, including eutrophication of surface water supplies, significant soil loss, and expanding coastal “dead zones.” These regions of hypoxia and fish mortality, exemplified by the Gulf of Mexico near the outflow of the Mississippi River, are likely caused by fertilizer runoff from agricultural practices in the Great Plains and the Midwest of the United States (see Wetzel et al. 2001 for an excellent review).

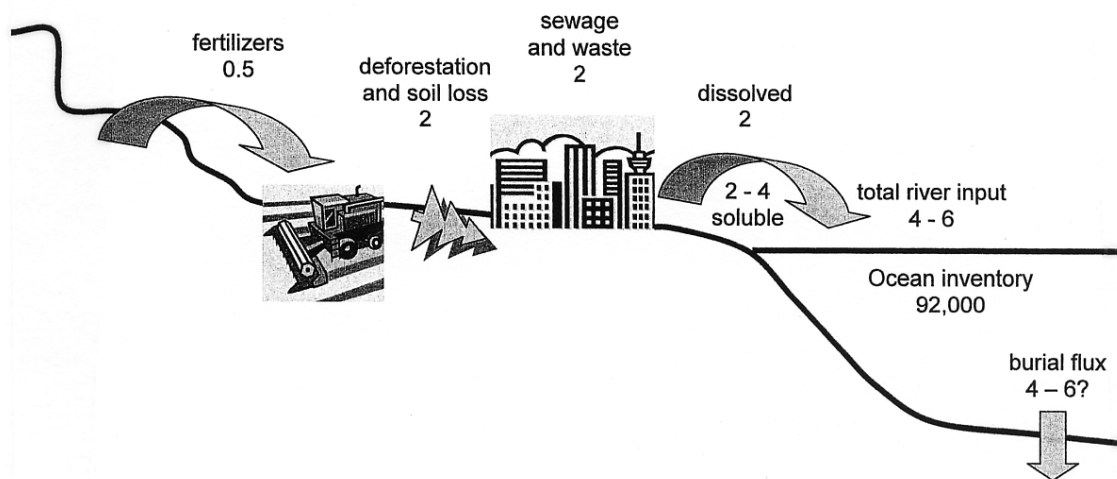


Figure 4. The modern (syn-human) phosphorus cycle, showing reservoirs (in Tg P) and fluxes (denoted by arrows, in Tg P/yr) associated with human activities, which have effectively doubled the natural dissolved P fluxes (cf. Fig. 1).

The net increase in dissolved-P release from land due to human activities also includes deforestation (plus concurrent soil loss), sewage, and waste sources (Fig. 4). Deforestation, typically by burning after selective tree harvesting, converts the standing stock of P in plant matter to ash. This P is rapidly leached from the ash and transported as dissolved loads in rivers; this transfer can happen on timescales of a year or two (Schlesinger 1997). Furthermore, the lack of rooted stability on the landscape results in

the loss of the relatively organic P-rich O and A soil horizons from many of these areas, from which some of the P is solubilized during transport. Sewage and waste are additional anthropogenic contributors to the terrestrial P cycle. Human waste, waste from processing of foodstuffs, and waste from industrial uses of detergents (which now are generally low-P but in the past contained up to 7 wt % P) contribute roughly equally to deforestation and soil loss.

The syn-human terrestrial P cycle (Fig. 4), therefore, is substantially different from the pre-human cycle (Fig.1). This is evidenced by high loads of dissolved P in rivers (about 2× estimated natural values) and higher loads of P-bearing particulates. Together, the net input of dissolved P from land to the oceans is 4-6 Tg P/yr, representing a doubling of pre-human input fluxes. As noted previously, this increased flux of P does influence coastal regions directly via eutrophication, but presumably an impact will be seen on the whole ocean. One likely scenario is that the P output flux and the oceanic P reservoir will both increase in response to higher inputs. This effect will be minimal, however, given the limited sources of P available for exploitation (one projection indicates the depletion of phosphate rocks as fertilizer sources by 3400 AD; Filippelli 1995) and the relatively long residence time of P in the ocean (about 15-30 kyr: Ruttenberg 1993, Filippelli and Delaney 1996, Colman and Holland 2000).

ECOSYSTEM DYNAMICS AND SOIL DEVELOPMENT

The effect of climate and soil development on P availability has been a focus of several excellent papers (Walker and Syers 1976, Gardner 1990, Crews et al. 1995, Cross and Schlesinger 1995, Vitousek et al. 1997, Schlesinger et al. 1998, Chadwick et al. 1999). For the most part, these studies have used P extraction techniques to determine the biogeochemical forms of P within soils. These techniques differentiate P in similar fractions, as displayed in Figure 2 (e.g., Tiessen and Moir 1993). The extraction techniques have been applied to depth and age profiles in soils to assess the rate of soil P transformations, the role of climate on these processes, the bioavailability of P in these systems, and the limiting controls on plant productivity. As the current geochemical state of a given soil is an integration of all conditions acting since soil development, most efforts have focused on settings in which climate is likely to have been constant (i.e., tropical settings), and the beginning state of the system and its age are very well known (i.e., soil developing on lava flows). These studies have thus made the classic substitution of space for time, with all the inherent assumptions of constancy in climate and landscape history.

Another approach to assessing terrestrial P cycling is to examine P geochemistry in lake sediments, using the same extraction techniques as the soil studies. This technique adds several dimensions to the soil work outlined above. First, lake sediment records allow us to examine an integrated record of watershed-scale processes associated with P cycling on the landscape. Second, it allows discrete temporal resolution at a given site, providing an actual record of local processes including landscape stability, soil development, and ecosystem development. Third, it extends our understanding of terrestrial P cycling to alpine and glaciated systems. The soil chronosequence approach is not likely to be successful here because of the climatic and slope variability between various sites (i.e., no substitution of space for time is possible). This third dimension is perhaps the most critical in terms of the P mass balance, as the greatest degree of variations in climate have occurred in these settings, and thus they hold the key to understanding the terrestrial P cycle on glacial/interglacial timescales.

Several limitations also exist in this approach. First, the lake sediment records analyzed must be dominated by terrestrial input, with very little lake productivity (i.e.,

very oligotrophic) and/or diagenetic processes occurring in the lake sediments. This is critical because the clearest signal of the state of soils in the surrounding landscape will come from a lake receiving this sediment as the primary source. This situation holds for numerous small lakes in headwater catchments, where local surface sedimentation dominates, dissolved nutrient inputs are so low that *in situ* organic production is at a minimum, and low amounts of labile organic matter in the sediments limits the degree of diagenetic overprinting on the original sediment record. Lowland lakes that integrate several watersheds and streams have a complex sedimentation history, and often have high rates of *in situ* productivity because of high nutrient inputs. Thus, these lakes are poor candidates for this approach. However, carefully chosen headwater lakes that characterize a relatively large range in climatic conditions, bedrock lithologies, and local landscape relief will provide important information on the weathering processes of P on land.

Example of the lake history approach to terrestrial P cycling

We have applied the lake sediment approach described above to several settings, and have found exciting results with important implications for the effects of climate and landscape development on the terrestrial P cycle. In a recent study (Filippelli and Souch 1999), we analyzed sediments from several small upland lakes in headwater catchments, selected to represent contrasting climates and glacial/postglacial histories. The longest records (about 20,000 years) came from two different lakes in the western Appalachian Plateau of the mid-western US: Jackson Pond, in central Kentucky (289 m above sea level), and Anderson Pond, in north-central Tennessee (300 m above sea level). Climate has strongly affected the ecological development of both of these systems (Delcourt 1979, Mills and Delcourt 1991, Wilkins et al. 1991), although neither was directly glaciated. In contrast, a 11,500 year record from Kokwaskey Lake in British Columbia (1050 m asl), clearly reveals the deglacial history of the region and retains the effect of alpine glaciers throughout the record (Souch 1994).

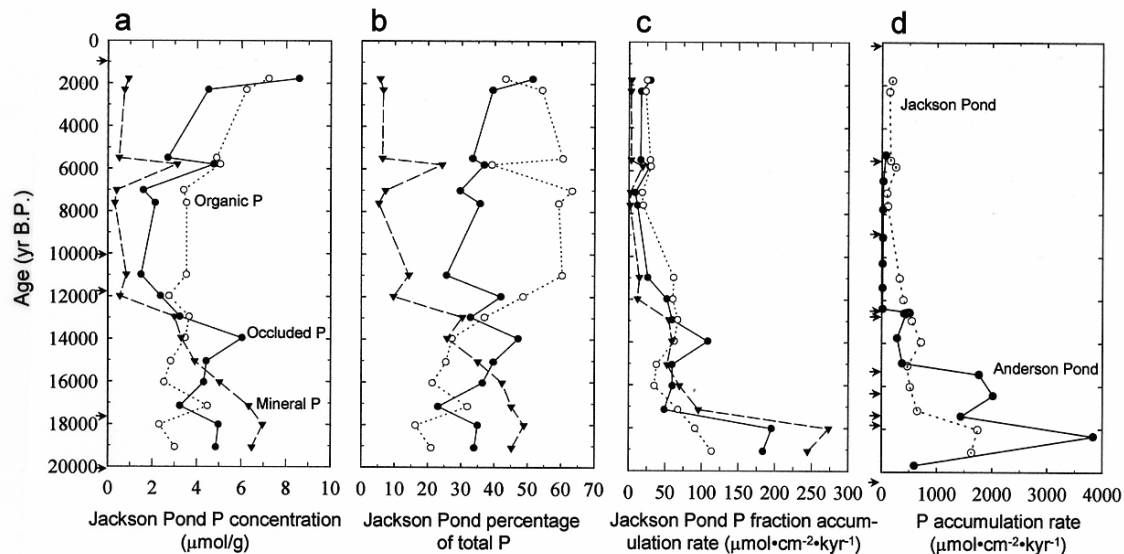


Figure 5. (a) P concentration and (b) percent of total P for each P-bearing fraction in sediments from Jackson Pond. (c) Accumulation rate of P fractions at Jackson Pond. (d) Total P accumulation rate at Anderson Pond and Jackson Pond. ¹⁴C age-control points for Jackson Pond (Wilkins et al. 1991) are shown as arrows on age axis in (a). Lowermost point is 20,330 yr. ¹⁴C age-control points are also shown for Anderson Pond (Delcourt 1979, Mills and Delcourt 1991) as arrows in (d). Lowermost point is 25,000 yr. The nonoccluded fraction (Fig. 2) is small and is combined with the occluded fraction in this analysis.

The geochemical profile for Jackson Pond reveals extreme changes through time (Fig. 5). In the early part of the record, marked by full glacial conditions (Wilkins et al. 1991), mineralized P was the dominant form entering the lake, with occluded and organic forms of lesser importance. During this interval, the landscape was marked by thin soils, high surface runoff, and closed boreal forests (Wilkins et al. 1991). With landscape stabilization and the onset of soil development (17 ka to 10 ka), the dominant forms of P entering the lake changed significantly, marked by a decline in the proportion of mineralized P and an increase in organic P (occluded P varied but exhibited no clear trend with age during this interval). In this interval, the closed boreal forests gave way to more open boreal woodland and a rapidly thickening soil cover (Wilkins et al. 1991). From the early mid-Holocene to the present, the concentration of mineral P shows little variation, while that of organic P and occluded P increased. Meanwhile, the ecosystem became dominated by deciduous hardwood forests and grasses, and a thick and stable soil existed (Wilkins et al. 1991). In terms of the percent of total P reflected by each fraction, the early Holocene marks a stabilization of the system to one dominated by organic and occluded P. By comparison, the concentration of mineral P is higher throughout the Kokwaskey Lake record, with occluded P of secondary importance and organic P in relatively low concentrations (Fig. 6). Mineral P exhibits a decrease during the interval of landscape stabilization and soil development (between about 9 and 6 ka), while the proportion of occluded P, and to a lesser extent organic P, increase during this interval. From the mid- to late- Holocene (6 ka to 1 ka), characterized by cooler/wetter conditions (Pellatt and Mathewes 1997), each fraction varies slightly. The last 1,000 years of this record, marked by the most extensive Holocene neoglaciation activity (Ryder and Thompson 1986), is characterized by a rapid return of P geochemistry to glacial/ deglacial conditions. Throughout the record, the ecosystem in this site is dominated by boreal forest, where slopes are steep, relatively unstable, and have much thinner soils than in the western Appalachian example.

These two examples suggest several controlling factors on P geochemical cycles.

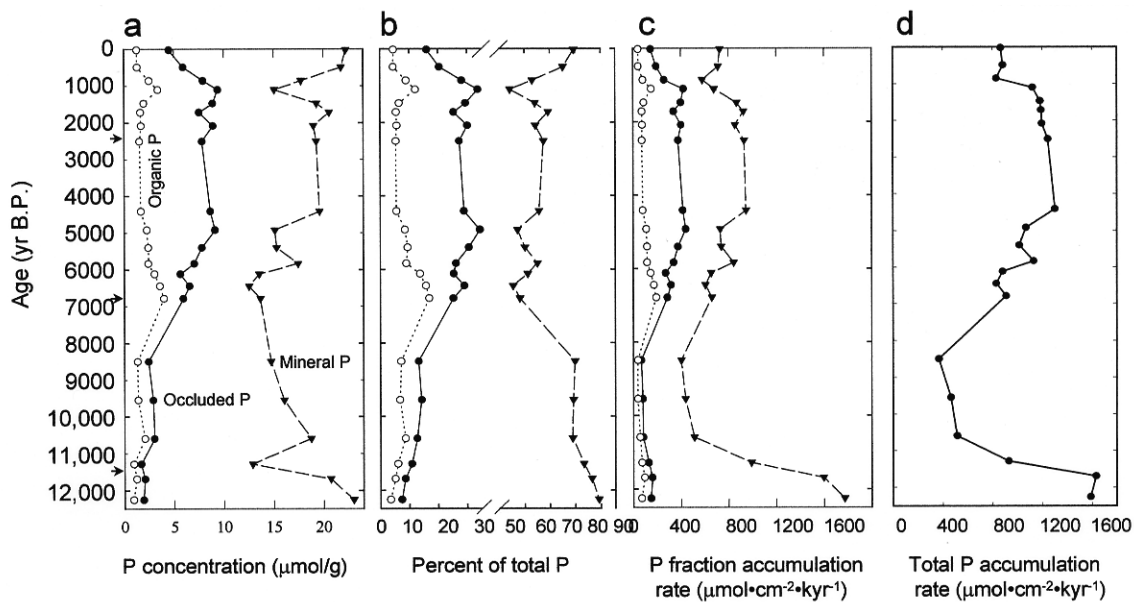


Figure 6. (a) P concentration, (b) percent of total P for each P-bearing fraction, (c) accumulation rate of P fractions, and (d) total P accumulation rate in Kokwaskey Lake sediments. Age-control points (Souch, 1994) are shown as arrows on age axis in A; the lowermost point represents a ¹⁴C datum, and the other two points indicate tephra dates (Mazama and Bridge River).

First, the transformation of mineral P to other (more bio-available) forms is more complete in a relatively wet, warm, and low relief system like western Appalachian than in a wet but cold and high relief system like the Coast Mountains. Thus, mineralized P decreases from 50% to 5% of total P at Jackson Pond compared to 90% to 50% at Kokwaskey Lake. This is consistent with the primary importance of physical weathering and erosion in the highly unstable environment in the Coast Mountains of British Columbia. Second, the relative starting points and stabilization points of these two systems are drastically different, driven by their contrasting landscape history and stability. Kokwaskey Lake was completely glacier covered at 12 ka, and thus the initial starting point for this system is nearly completely mineral P from rock flour. Throughout the Holocene, the high relief in the watershed led to constant loss of surface sediments with poorly developed soils and relatively little organic P. In contrast, low relief and relatively rapid development of a stabilized landscape and soil profiles in the Jackson Pond watershed supports the development of a mature soil in terms of P geochemistry. Additionally, because the Jackson Pond watershed started with a climate and ecosystem similar to that of Kokwaskey Lake during the interval from 6 ka to 1 ka, their comparative P geochemistries are similar in these intervals. The model presented earlier (Fig. 2) is therefore useful for tracking soil P transformations from the lake cores presented here. For the western Appalachian setting, the soil system begins in a slightly pre-weathered stage, and progresses to an end-point dominated by the organic and occluded fractions (Fig. 2). For the alpine setting, the soil system begins as rock flour, and shifts slightly toward more developed P forms as warming and more landscape stabilization occurs in the mid-Holocene followed by extensive neoglaciation over the last 1,000 years (Fig. 6). Finally, the P geochemistry of these systems can be reset quickly. During the last 1000 years, readvance of alpine glaciers during the Little Ice Age has been sufficient to return the P geochemical cycle in this region back to near glacial conditions (Fig. 6).

Patterns in P weathering and release are similar to those observed in several tropical settings. For example, a chronosequence of Hawaiian soils reveals significant transitions in mineral P after about 1,000 years of soil development (Crews et al. 1995, Vitousek et al. 1997), while significant transformations occur in P biogeochemistry during soil development on a Krakatau lava flow in just over 100 years (Schlesinger et al. 1998). In the temperate settings presented here, this decrease occurs over timescales of 3,000 to 5,000 years. One of the key differences is that the temperate settings are periodically reset due to glacial climate conditions. This resetting keeps these soil systems in a 'building phase.' But like the tropical environments, the progressive loss of P during soil development leads to P limitation to terrestrial ecosystems.

Large changes in the accumulation rate of P over time are reflected in all the lake records. These accumulation rate changes are driven partly by changes in bulk sedimentation rate, but several of the rapid shifts in P accumulation occur between age control points and thus are not driven just by rates of sedimentation. The two western Appalachian sites reveal a rapid pulse of P input during the glacial and initial deglacial interval (Fig. 5), a period of enhanced colluvial activity when soil development was just commencing. Upon landscape and soil stability (by 10 ka), P inputs had decreased 10-40 fold, and remained low and constant to the top of the record (2 ka). The Kokwaskey alpine site also reveals significant changes in P input (Fig. 6), beginning with a rapid early deglacial pulse consisting mainly of mineralized P originating from glacial rock flour. From approximately 9 to 6 ka, landscape stabilization begins, although the landscape is still marked by high relief and rapid rates of erosion. Phosphorus input rates are high but decrease slightly from 4 to about 1 ka. In this high relief, alpine setting, soil development is retarded by rapid denudation, and thus the terrestrial P cycle is stuck in an

'initial development stage' with high mineral P and high P release rates from the landscape.

Although the temporal records differ between the sites, some generalizations may be made about terrestrial P cycling, climate, and landscape development as a function of glacial/interglacial cycles. First, the lake records reflect input of solid-phase P released from watersheds. Some portion of this released P is bioreactive in terrestrial systems and upon transport, also bioreactive in the ocean. The P geochemical results indicate that the more bioreactive forms dominate in later stages of soil development. However, this increase in the bioreactive nature of the P is offset by very low total P release at these times, as reflected by the total P accumulation rate records from the lakes. In the case of dissolved phosphate, we relate the initial stage of soil development to high solid-phase loss that also likely leads to a relatively poor recycling of the dissolved phase (from a lack of oxide-bound occluded pools), a so-called 'leaky ecosystem.' Second, the western Appalachian sites have reached a degree of landscape stabilization due to relatively stable climates. Although the elevation, local relief, mean temperature, rainfall, and ecosystem are quite different for these sites, the net result of soil stabilization is to reduce the rate of P loss from these systems. The alpine British Columbia site, on the other hand, has never achieved the relative stabilization of the other sites due to high relief and neoglacial activity. Thus, the trends in P release from this system lags, and P release remains relatively high and constant. We believe that the results presented here characterize mid- and high- latitude watersheds that have been directly glaciated or strongly affected by proximal glacial conditions. Tropical environments may experience less dramatic climate change through glacial/interglacial intervals, but recent terrestrial evidence reveals that even these systems experience notably cooler and drier conditions during glacial intervals (Thompson et al. 1997), which may lead to changes in the extent of soil development and P release in these systems as well.

The lake sediment records presented here indicate a terrestrial P mass balance that is not near steady state on glacial/interglacial timescales, with important implications for the functioning of terrestrial and oceanic systems. Coupling these records of solid-phase P changes over time with oceanic records of dissolved inputs from rivers will eventually provide important constraints for the influence of climate on chemical weathering and the global P cycle.

CONTROL OF OXYGEN ON COUPLED P AND C CYCLING IN CONTINENTAL MARGINS: A CASE STUDY FROM THE ANOXIC SAANICH INLET

Uncertainty currently exists about the removal of C and P from the oceanic reservoir. The ratio of organic C (C_{org}) to organic P (P_{org}) in sediments is a critical parameter in many paleoceanographic and paleochemical models (Holland 1984, Sarmiento and Toggweiler 1984, Delaney and Boyle 1988, Boyle 1990, Delaney and Filippelli 1994, Van Cappellen and Ingall 1994, 1996), with estimates of the global average C_{org}/P_{org} in marine sediments ranging from 367 (Williams et al. 1976) to 496 (Ramirez and Rose 1992), with at least a 70% range on each of these averages. Also, these values contrast with the value of about 106 in marine organic matter (e.g., Redfield et al. 1963), which is the dominant source of organic C and P to the marine sediments. Several recent studies suggest that P may exhibit a significant preferential regeneration compared to C during diagenesis of organic matter in low oxygen continental-margin sediments (Ingall et al. 1993, Compton et al. 1993, Ingall and Jahnke 1994, Schenau et al. 2000). If true, decoupling of these elements may occur in their long-term biogeochemical cycles (Van Cappellen and Ingall 1994, 1996). As noted by Colman et al. (1997), accurate measurements of this ratio in a variety of marine settings are required to fully understand

coupled C and P cycling and burial, and much controversy still exists as to the viability of the preferential regeneration model for P (e.g., Anderson et al. 2001).

Recent research on the P geochemistry of both deep-sea (Filippelli and Delaney 1996, Delaney 1998) and continental-margin sediments (Ruttenberg and Berner 1993, Filippelli 2001) suggests that a better understanding of the diagenesis of P in sediments may help to resolve many questions concerning what happens to P and C after burial. Several diagenetic transformations of P have only recently been detected (Fig. 7). First, organic P concentrations in sediments decrease dramatically with both depth and age; values at depth typically are less than 10% of near-surface values (Filippelli and Delaney 1996). These decreases are probably caused by microbial regeneration of organic matter and release of P from its organic form. Based only on these results, a net loss of P from the sediments may be assumed. However, concurrent with the decrease in reactive forms of organic P is an increase in authigenic P in the sediments. Authigenic P most likely occurs as carbonate fluorapatite (CFA), an authigenic mineral that forms predominantly in continental margin sediments under regions of high primary productivity (Kazakov 1937, Veeh et al. 1973, Burnett et al. 1982, Froelich et al. 1982, Baturin 1988, Garrison and Kastner 1990, Filippelli and Delaney 1992, Filippelli et al. 1994, Schuffert et al. 1994, Reimers et al. 1996, Kim et al. 1999), but has also recently been identified in non-upwelling continental-margin sediments (O'Brien and Veeh 1980, Ruttenberg and Berner 1993, Berner et al. 1993, Lucotte et al. 1994, Kim et al. 1994, Krajewski et al. 1994) and even in deep-sea sediments (Filippelli and Delaney 1996).

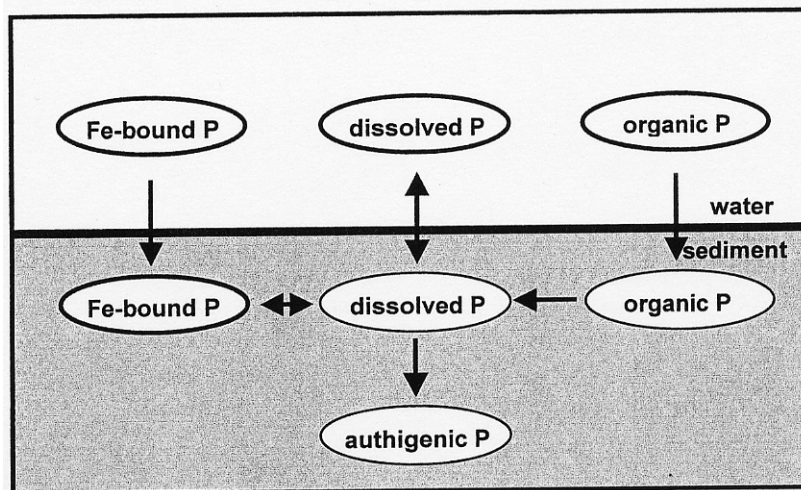


Figure 7. A conceptual diagram of P geochemistry in oceanic sediments (from Filippelli and Delaney 1996). Phosphorus associated with organic matter is the primary source of P to the sediments, although the depositional flux of Fe-P is commonly similar to that of organic P in continental margin settings. Organic matter degradation leads to the release of P to interstitial waters. Dissolved P in interstitial waters appears to be involved in several processes, including adsorption to grain surfaces, diffusion back to bottom waters, binding to iron oxyhydroxide minerals (which also scavenge some P from deep waters during particle formation in the water column), and incorporation in an authigenic mineral phase. In Saanich Inlet, the most important burial sink for P is the authigenic component, where P is probably mineralized authigenically as carbonate fluorapatite (CFA).

The increase in authigenic P with depth largely offsets the decrease in organic P, resulting in limited loss of P compared to C in sediments after burial below the sediment-water interface (Fig. 8). Important implications of these results include:

- (1) Organic P is altered in marine sediments during diagenesis, but P is redistributed within the sediments to other burial pools rather than lost.

- (2) Because Porg decreases, post-diagenetic Corg to Porg ratios may be higher than pre-diagenetic ratios. This increase, however, may not represent real changes in total organic C to reactive P ratios in sediments because of the transfer of P into other burial pools.
- (3) Previous studies have assumed no fractionation of Corg compared to Porg during diagenesis (Mach et al. 1987, Ramirez and Rose 1992); the diagenesis of Porg discussed above indicates that this might not be the case.
- (4) The variability in published Corg:Porg ratios in marine sediments may be due to sampling across zones of organic P diagenesis, the depth trends of which may vary from region to region depending on sediment type, original organic matter content, and sedimentation rate (e.g., Ruttenberg and Berner 1993, Filippelli and Delaney 1996).

Saanich Inlet, British Columbia

In this discussion, I will examine the cycling of C and P and C:P ratios in sediments from the anoxic Saanich Inlet (located near Victoria on Vancouver Island, British Columbia, Canada). This basin was cored by Ocean Drilling Program (ODP) Leg 169S in 1996 at two sites (Bornhold et al. 1998). The blue-gray silty sediments in the lower part

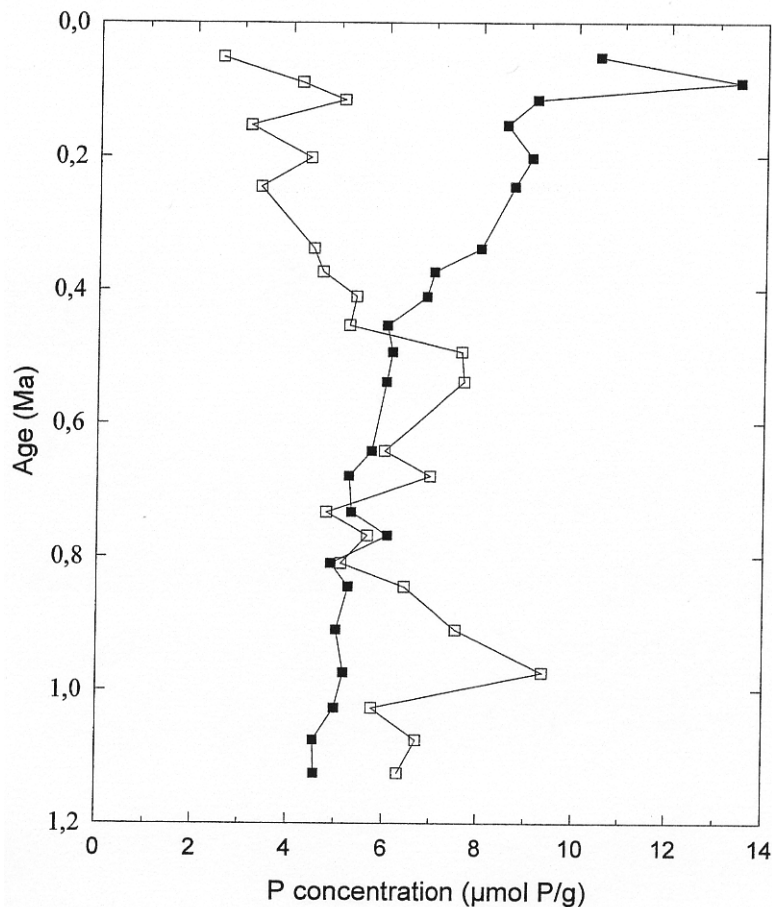


Figure 8. Detailed view of phosphorus geochemistry at Leg 138 Site 846B, eastern equatorial Pacific, for the past 1.2 Myr. (From Filippelli and Delaney 1996). Authigenic component (\square) and the sum of the other reactive components (\blacksquare , including adsorbed, iron-bound, and organic phosphorus) versus age, showing decreases in other reactive forms offset by increases in the authigenic component.

of the cores reflect the input of glacially derived material from regional and local deglaciation. Clear laminations begin about 9,000 years ago and persist in the basin from about 7,000 years ago to present. This transition marks the onset of mainly marine sedimentation and extreme sill-controlled restriction of circulation in the Saanich Inlet, which resulted in anoxia. The laminations are varves, exhibiting seasonal stratification related to winter runoff and spring and summer biological blooms (Dean et al. 2001, Johnson and Grimm 2001), from which annual-scale sedimentation rates can be determined. The average rates of sedimentation are quite high (up to 2.5 cm/year), and thus accumulation rates of organic matter are high. These factors make the Saanich Inlet cores recovered during ODP Leg 169S excellent end-member examples of coupled C and P cycling. Results presented here reveal that although Corg:Porg ratios are high and increase with depth, this effect is due largely to a remobilization of P from an organic matter sink to an authigenic sink. Reducible sedimentary components act as temporary shuttles in this process even in this anoxic setting, with the ultimate burial sink for the remobilized P being carbonate fluorapatite. The effective ratio of organic C to reactive P (the sum of P-bearing sedimentary components considered potentially chemically reactive in marine settings) appears to be about 150-200, indicating some preferential loss of P compared to carbon during organic matter degradation, but not approaching previously reported values of over 3,000 in black shales (e.g., Ingall et al. 1993). Reactive P burial rates in this basin range from 10,000-60,000 $\mu\text{mol}/\text{cm}^2/\text{kyr}$, greatly exceeding the range of 500-8000 $\mu\text{mol}/\text{cm}^2/\text{kyr}$ found in most continental margin settings, including regions of modern phosphogenesis (Filippelli 1997a).

Age determinations were made based on the ^{14}C stratigraphy developed for this site (Blaise-Stevens et al. 2001). A variety of high-resolution carbon and isotopic records were also produced for this site (Calvert et al. 2001, McQuoid and Whiticar 2001). In order to develop geochemical accumulation rate estimates that take into account real sedimentation variability in this setting, I used a different technique to calculate sedimentation rates. The laminations preserved in this core are annual, an interpretation based on years of box and piston core work in this setting. Using core photos, I measured the lamination width within the 10 cm span of each sample location used in this study and reported this average lamination width as the sedimentation rate. Thus, instantaneous sedimentation rates are used for calculations of P accumulation rates instead of sedimentation rates averaged over large age control ranges.

Organic carbon and phosphorus geochemistry

Organic carbon concentrations are high in the upper marine-dominated sediments and decrease with increasing depth and age, ranging from 2.0-2.4 wt% at the surface to 1.2-1.8 wt% at 7,000 years ago (Fig. 9). This decrease continues to the base of the cores, and very low organic carbon values are found in the terrigenously derived clays near the lower portions of the cores, with values as low as 0.2 wt%. Values are consistently higher in the shallower Site 1033 by about 0.3 wt%. The uppermost sample at Site 1033 is relatively low (0.9 wt%) and deviates from the general trend of the other organic-rich samples near the surface. Organic P values decrease with increasing age and depth, ranging from values of 4-6 $\mu\text{mol}/\text{g}$ at the surface to 1-2 $\mu\text{mol}/\text{g}$ at depth (Fig. 9). This decrease virtually parallels that of Corg, although the decrease in Porg with depth and age is more rapid than that of Corg (Fig. 9). It should be noted that for these two sites, with different average rates of sediment accumulation, geochemical trends with age match, whereas trends with depth do not. This indicates that organic matter degradation, the dominant factor driving these geochemical parameters, is related to sediment age and not depth. This further implies that the process of organic matter degradation is kinetically controlled rather than diffusively controlled at this site.

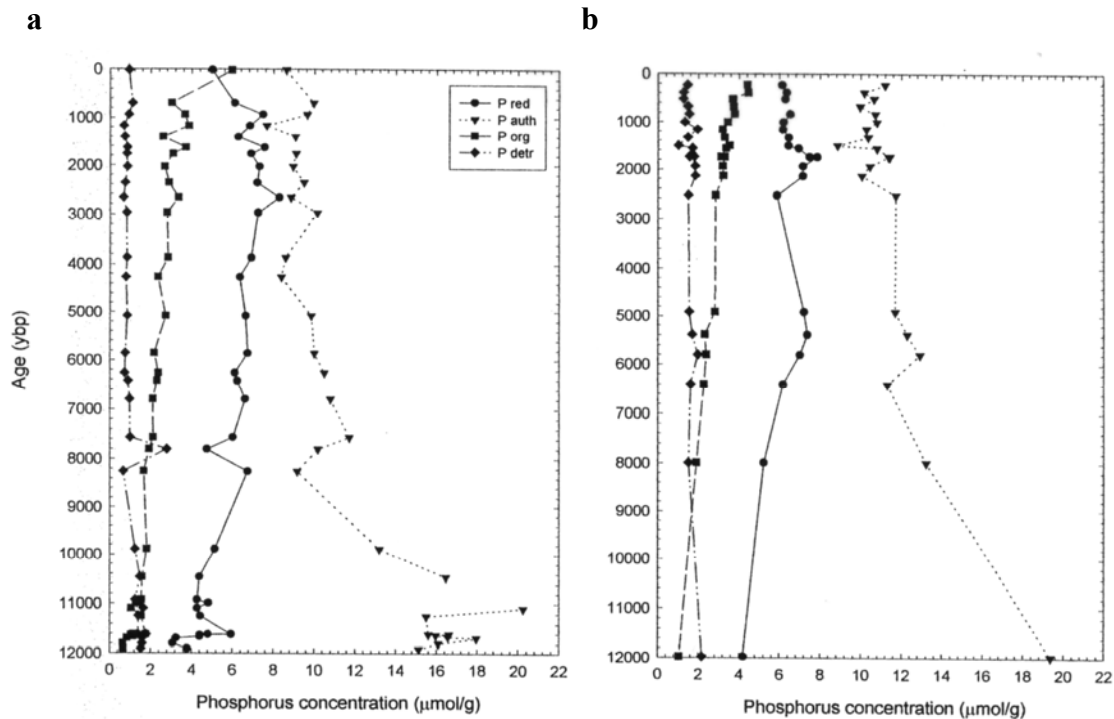


Figure 9. Geochemistry of P with age at Sites 1033 (a) and 1034 (b). The geochemical fractionation was performed via a sequential extraction technique (Ruttenberg 1992, Filippelli and Delaney 1996, Anderson and Delaney 2000), which separates reducible and adsorbed phases (P red), authigenic phases (likely CFA--P auth), organically-bound P (P org) and detrital P (P detr). Note an overall decrease in the reducible and organic fractions and an increase in the authigenic fraction in the older sediments.

The molar ratio of Corg:Porg is elevated compared to the values of Redfield et al. (1963) throughout the Saanich Inlet record (Fig. 10). Values as high as 800 exist in the lower marine-dominated sediments. Corg:Porg ratios decrease in the younger sediments, approaching projected values of 150-250 in surface sediments (note that a true sediment/water interface was not successfully recovered in these cores due to the soupy nature of the sediments, and the youngest sample shown for Site 1033 is likely a composite of sediments deposited over the last century). Relatively high values of 400 are seen in the glacially-derived clays in the older sections, likely reflecting typical Corg:Porg ratios in terrestrial soils and sediments (Schlesinger 1997).

The increase in Corg:Porg ratios with depth and increasing age could be interpreted to represent a net loss of P in comparison to carbon from the sedimentary sink in this environment. Certainly, the values greater than Redfield et al. (1963) projected even for the surficial sediments indicate a small preferential loss of P from this system during organic matter degradation, supported by P flux measurements in this and other margin settings (e.g., Murray et al. 1978, Ingall and Jahnke 1994, 1997; McManus et al. 1997, Colman and Holland 1999). The Corg:Porg ratios for surficial sediments found here are much lower than those determined for several other anoxic settings, indicating that preferential release of P may not occur to the extent previously suggested in anoxic settings (e.g., Ingall et al. 1993; note, however, that this study was performed on black shale in the rock record, not modern marine sediments). It should be noted, however, that the Saanich Inlet is an end-member example of marginal sedimentary environments due to its extremely high sedimentation rates. Furthermore, organic matter degradation is very rapid in this setting, and ODP-type coring will not be able to capture a true snapshot of

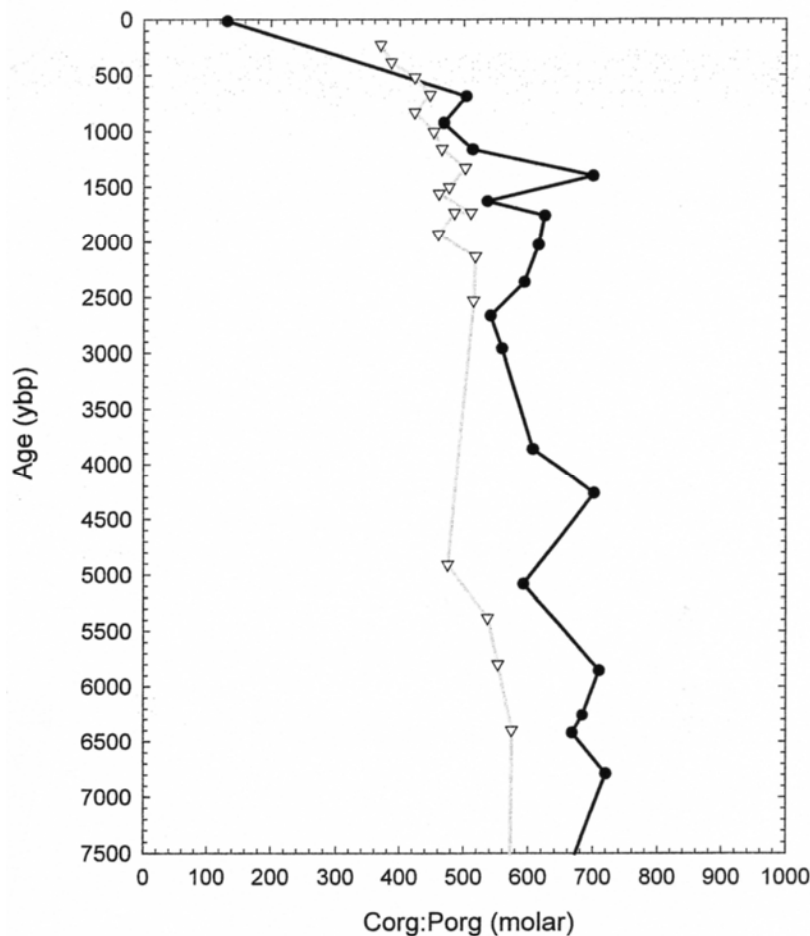


Figure 10. Corg:Porg ratio (molar) with age at Sites 1033 (●) and 1034 (Δ) in the Saanich Inlet. This ratio increases sharply over the first ~2,000 years of the record, driven by the redistribution of P to authigenic phases with no net loss from the sediment column.

the geochemical cycles of C and P on timescales of years to decades in surface sediments, because of the soupy nature of these sediments and their disturbance due to blow-off during coring. Present efforts at box-coring coupled with benthic chambers may be the most fruitful approach for this purpose.

The increase in Corg:Porg ratios with depth and age (Fig. 10) is the result of preferential loss of P compared to C from organic matter. However, the P released from organic matter is not simply lost as a benthic dissolved flux. Instead, this P is incorporated into several other sedimentary phases with a net retention of total reactive P (Fig. 11). At shallower depths and younger ages, the released P is adsorbed onto reducible iron and manganese-bearing phases. This is supported by the initial increase in reducible-related P as well as by peaks in iron and manganese released from a reductant treatment. Iron oxyhydroxides can coprecipitate a large amount of phosphate due to their large surface areas (~500 m²/g) and numerous delocalized charges (Froelich 1988, Feely et al. 1990). Iron redox cycling in sediments appears to be a strong control on benthic P retention and release, with disseminated iron oxyhydroxides acting as a temporary shuttle in the interface between oxic and iron-reducing zones within continental margin and deep sea sediments (Sundby et al. 1992, Lucotte et al. 1994, Filippelli and Delaney 1996). The presence of reducible iron phases with depth in anoxic sediments has been verified by Canfield (1989). The exact nature of this reducible phase is debatable. The ferric phases

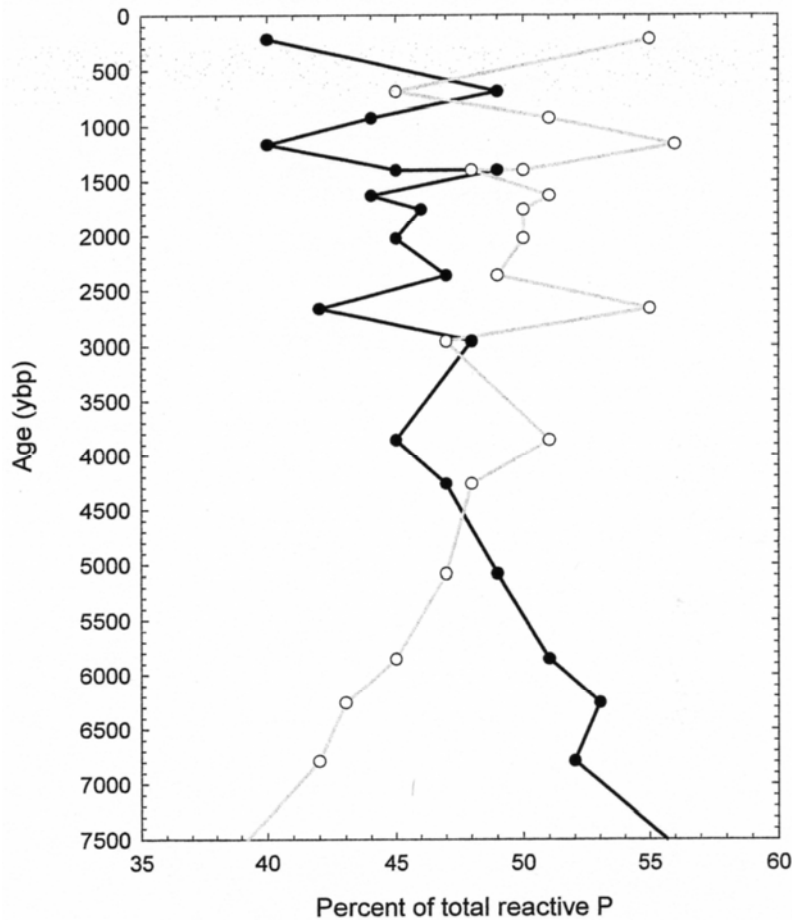


Figure 11. Percent of total reactive P in this authigenic phases (filled circles) and in the reducible and organic phases (open circles) for Site 1033. This comparison reveals the sink-switching that occurs during sedimentary P cycling, with the ingrowth of an authigenic P phase and a loss of P from other reactive phases with age and depth.

documented by Canfield (1989) were well crystallized and likely relatively low in P. It is not likely that amorphous oxyhydroxides, which are important for adsorbing/co-precipitating P in oxic settings, are contributing at depth in this anoxic setting: Reimers et al. (1996) found little or no ferric oxyhydroxides below 6 cm in sediments from the anoxic Santa Barbara Basin. It could be argued that the aggressive reducing agent used in this extraction (buffered citrate dithionite bicarbonate solution—CDB) can partially dissolve iron silicates, although this would lead only to elevated iron and not to the observed P enrichment (due to the low concentration of P associated with iron silicates). Regardless of the exact nature of the reducible pool, it appears only to be a relatively temporary sink for P. At greater depths and ages, P is lost from the reducible phase and incorporated into an authigenic P-bearing mineral phase. This authigenic phase is likely carbonate fluorapatite (CFA), a suggestion supported by depletion in pore water fluoride at depth in the Saanich Inlet cores (Mahn and Gieskes 2001) and, as previously mentioned, documented in several other marine settings. Interestingly, CFA appears to form slowly and at relatively great depth in the Saanich Inlet compared to the Santa Barbara Basin, where porewater chemistry indicates that CFA growth is restricted to the upper few centimeters (Reimers et al. 1996).

In a marginal setting like the Saanich Inlet, changes in depositional characteristics of P have to be considered along with diagenetic remobilization of P. For example, how

much do the down-core records of organic P reflect changes in the chemistry of the continental input? It appears that for this setting, all of the changes in P chemistry observed are driven by internal (diagenetic) processes rather than external (depositional) processes. This bold statement can be made because we have also examined the dynamics of terrestrial P weathering in this region. As noted previously, we analyzed down-core P geochemistry in a sediment core from Kokwaskey Lake, a headwater lake of the Kwoiek watershed in the Coast Mountains of British Columbia, just east of the Saanich Inlet (Filippelli and Souch 1999). We found an increase in the fraction of organic P weathered from the landscape from 12,000 - 8,000 years ago in response to soil development, nearly constant values until about 1,000 years ago, then a sharp decrease in organic P over the last 1,000 years in response to the Little Ice Age and neoglacial advances. In comparison, the organic P record from the Saanich Inlet shows an increase over the last 7,000 years, and not the constant values followed by a sharp decrease we would expect if this record was driven primarily by depositional processes.

Phosphorus burial

Short-term versus long-term burial. Because of active diagenesis of organic matter in the Saanich Inlet, several aspects of C and P burial must be considered. The longer records presented above speak to issues of C and P burial on long (~1,000 to 10,000 yr) timescales. This is a critical parameter for understanding the role of continental margins for storing these components in terms of glacial/interglacial mass balances and climate, and will be addressed in the next section. The very active processes occurring at the sediment-water interface, however, are not addressed by the long-term burial trends. Thus, it might be instructive to compare long-term burial with instantaneous measurements of the reflux of dissolved phosphate from sediments back to the water column.

Pore water determinations and benthic flux chamber experiments can both provide insight into how P cycling relates to organic matter degradation occurring in the surface tens of centimeters to several meters of sediment. For pore water determinations, the concentration of dissolved phosphate is determined from pore water squeezed from numerous depth intervals. Trends in the pore water phosphate concentration with depth can be modeled using diffusion models, typically related to organic matter degradation, and these modeled trends can be used to estimate the flux of dissolved phosphate out of the sediments. This type of analysis has been performed for P in a variety of settings, and is summarized comprehensively in Colman and Holland (2000). They find that P reflux from sediments is quite large in terms of oceanic mass balances, with high sedimentation rate, high C regeneration rate, and the redox state of the sediments enhancing P reflux from continental margin sediments. Given sedimentation rates for surface sediments in the Saanich Inlet, the P reflux would be about 0.2 mol P/m²/yr, based on the global relationship of Colman and Holland (2000). Murray et al. (1978) performed pore water chemistry on sediments from the Saanich Inlet sampled in April 1976. Using the sediment parameters from this study, which are quite similar to those for the ODP cores analyzed here, Colman and Holland (2000) calculated a seasonally averaged annual mean P reflux rate of 0.18 mol P/m²/yr. The long-term burial rates of P found in this study range from ~0.1 to 0.6 mol P/m²/yr. Thus, in a simplistic comparison, approximately 35-75% of the total reactive P reaching the seafloor is buried (i.e., 25-65% is released back to the water column). This assumes, of course, a predictable relationship between short-term and long-term burial processes. But as noted earlier, P remobilization and incorporation into authigenic phases appears to be the largest control on long-term P cycling, whereas P remobilization and reflux back to the overlying water column is the largest control on short-term P cycling. Although C and P cycling pathways during diagenesis are different, taken together, a benthic loss of 25-65% of the reactive P with little net change in the Corg:Preactive ratio indicates a substantial benthic loss of C as

well. This indicates that organic matter regeneration and C and P cycling are very active in anoxic settings, supporting suggestions by Pederson and Calvert (1990) and Calvert et al. (1992) to that effect.

Benthic flux chamber experiments measure the loss or gain of various dissolved species from a fixed container on the seafloor, thus yielding instantaneous measurements of P cycling. A benthic flux chamber deployment in the Saanich Inlet in summer, 1997

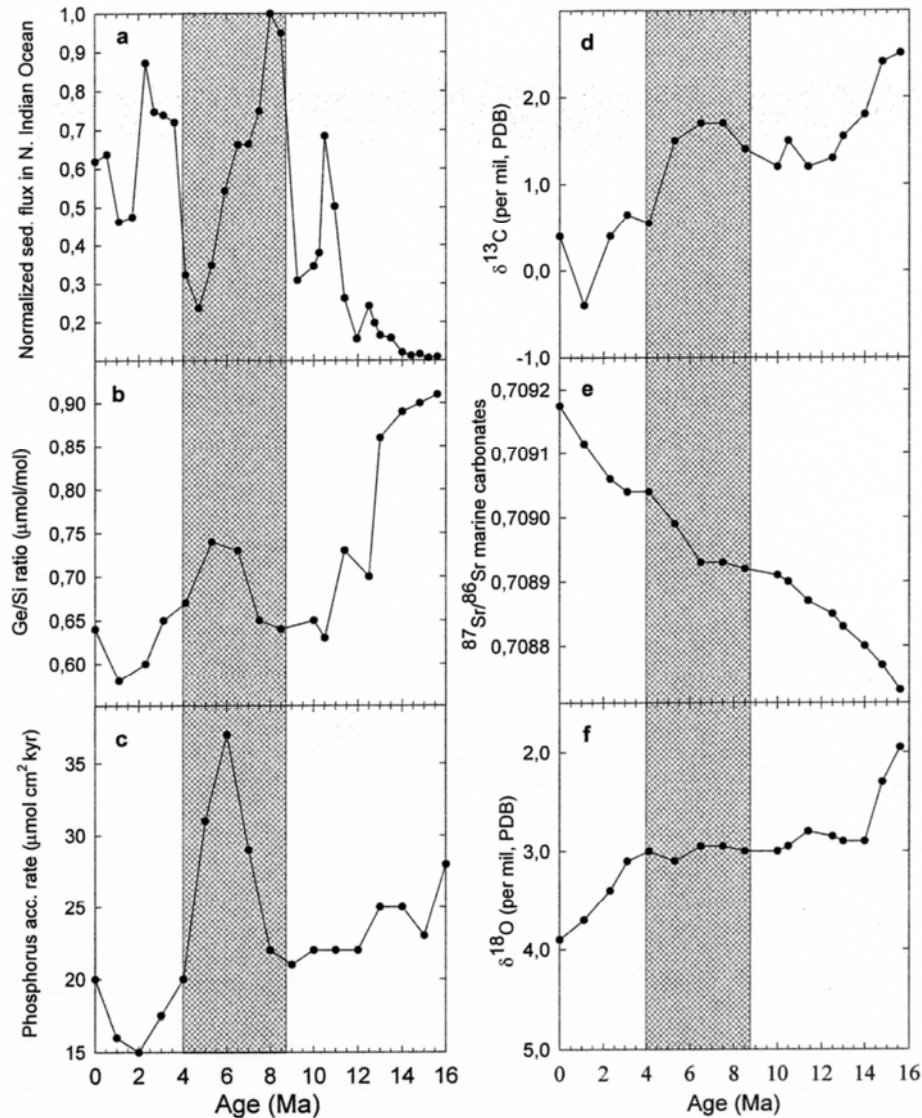


Figure 12. Sedimentary and geochemical records from oceans, showing dramatic transient shifts in most records in an interval from just before 8 Ma to 4 Ma (shaded), from Filippelli (1997b). Symbols in all records represent averages of 1 Myr intervals, except for normalized sediment flux curve, which represents 0.5 Myr averages. After interval averaging, all records were adjusted to time scale of Cande and Kent (1992) for consistency. (a) Normalized sediment flux in northern Indian Ocean (Rea 1992). (b) Ge/Si ratio in opaline silica from diatoms (Shemesh et al. 1989). (c) $\delta^{13}\text{C}$ of bulk marine carbonates (Shackleton 1987). Although details of different carbon isotope records differ, general trends revealed in this low-resolution record are robust. PDB is Pee Dee belemnite. (d) Phosphorus accumulation rates in equatorial Pacific (Filippelli and Delaney 1994). Peak in accumulation rates is also observed in other parts of Pacific (Moody et al. 1988) and western Atlantic (Delaney and Anderson 1997). These peaks are linked with increased phosphorus input rates from continental weathering (e.g., Filippelli and Delaney 1994). (e) $^{87}\text{Sr}/^{86}\text{Sr}$ record from marine carbonates (Hodell et al. 1990, 1991). (f) $\delta^{18}\text{O}$ of benthic foraminifera (Miller et al. 1987).

yielded a P reflux rate of ~ 2 mol P/m²/yr (E. Ingall and T. Lyons, pers. comm.). This is extremely high, compared to short-term rates of ~ 0.2 mol P/m²/yr, and compared to long-term burial rates would indicate that only about 5% of the reactive P reaching the seafloor is buried. More likely, this instantaneous summer flux is a pulsed release of P released from biogenic bloom detritus and represents a non-steady state cycling event. The degradation of the bloom detritus would contribute a significant amount of P related to organic matter. Rapid degradation could also result in a lowering of the redox boundaries in the upper several millimeters of the sediments, releasing some of the iron-bound P (e.g., Colman and Holland 2000). Note also that the bottom waters of the Saanich Inlet are seasonally oxic. This could lead to seasonal storage of P in a thin surficial layer of oxic sediment that would have fresh iron oxyhydroxides—formed by oxidation of pore water ferrous iron diffusing from the anoxic portion of the sediments. Coprecipitation and adsorption of phosphate could lead to a substantial amount of P in this thin layer. Rapid deposition of organic matter to the sediment following a bloom would not only be followed by rapid degradation and release of associated organic P, but could contribute to the release of any surficial oxyhydroxide-associated P. This kind of seasonal behavior for P diagenesis is well documented for Cape Lookout Bight sediments (Klump and Martens 1981).

Long-term P burial and the global P cycle. Continental margins are important burial sites for oceanic P. Margin sediments likely constitute between 50% and 80% of the total P removal from the ocean (e.g., Baturin 1988, Ruttenberg 1993, Filippelli 1997a, Schuffert et al. 1998, Compton et al. 2000), even given their small surface area compared to the deep ocean. As such, sedimentologic, tectonic, and eustatic influences on continental margins can greatly affect the oceanic P cycle. The Saanich Inlet is an end-member example of a dynamic continental margin setting, experiencing a sharp transition from glacial-terrigenous to marine sedimentation, silling of the outlet and restricted circulation, and local glacial rebound in the face of the eustatic sea level rise associated with deglaciation. The Saanich Inlet is also an end-member example of P burial, with accumulation rates of 10,000 to 60,000 $\mu\text{mol}/\text{cm}^2/\text{kyr}$, about 2 to 50 times that typically observed in continental margin settings (Filippelli 1997a). Although the Saanich Inlet is not a typical margin setting, it can serve to illustrate the extreme example of the effects of continental margin dynamics on marine P cycling during a glacial to interglacial (G/IG) transition. This may serve to help us link several G/IG records developed in the deep ocean (e.g., Murray et al. 1993, Latimer and Filippelli, 2001) with a new awareness of the dynamic nature of P cycling on land (Filippelli and Souch 1999).

The Saanich Inlet evolved rapidly from a basin that accumulated no reactive P from the marine reservoir during full glacial and deglacial time to one with extremely high reactive P accumulation by 7,000 years ago. High reactive P accumulation rates have persisted from 7,000 years ago to present, driven by intense biological blooms and very high sedimentation rates. This progression may mirror that of many continental margins, especially those at or above sea level at the last glacial maximum. In these settings, the locus of upwelling-induced productivity would be centered over deeper waters well off the continental shelf. Given that the major initial input of P to sediments is in the form of marine organic matter (with the exception of regions proximal to river outflows, where terrestrial organic matter and oxides are important additional sources; e.g., Berner and Rao 1994, Compton et al. 2000, Goñi et al. 1998), the additional sinking time and slower sediment burial at the sediment/water interface would increase the regeneration of P from this organic matter back to the water column. Thus, the net internal effect of lowered sea level would be to enhance P regeneration, reduce the continental margin sink for P, and increase P burial in the deep ocean sink (assuming steady state). Because of enhanced internal recycling, this process could also lead to a greater inventory (higher concentra-

tion) of P in the ocean. The few studies of P accumulation rates on G/IG timescales in deep sea sediments do indicate higher P accumulation rates during glacial intervals (e.g., Murray et al. 1993, Murray et al. 2000, Latimer and Filippelli, 2001), but these studies were performed in high productivity regions (the equatorial Pacific, the Southern Ocean) which respond strongly to changes in upwelling intensity. The only reliable proxy for P concentration in the ocean is the Cd/Ca ratio of foraminifera, which showed a slightly higher P concentration in the deep Atlantic waters during glacial intervals, but changed little in other basins (e.g., Boyle 1990). The whole scenario is further complicated, however, by the assumption of steady state input flux of P to the oceans and constant P cycling on continental margins on G/IG timescales. Neither assumption is good, and in fact we see quite large variations in terrestrial P cycling on G/IG timescales as the result of glaciation, soil, and ecosystem development (Filippelli and Souch 1999), and much has been said about margin-basin fractionation of nutrients on these timescales (e.g., Broecker 1982). More studies of C and P cycling and burial will need to be performed on a greater variety of continental margins to constrain the internal dynamics of the marine P cycle on G/IG timescales, with these results tied to deep sea and terrestrial records.

PHOSPHORUS AND MARINE PRODUCTIVITY ON CENOZOIC TIMESCALES

Ocean geochemical and sedimentological records are among the best evidence available for reconstructing past climates and weathering events on land. An intriguing hypothesis developed from studies of Cenozoic marine records is the Himalayan uplift hypothesis (e.g., Raymo et al. 1988, Raymo and Ruddiman 1992), which argues that the uplift of the Himalayan-Tibetan Plateau during the Cenozoic increased net continental-chemical weathering rates, increased drawdown of atmospheric CO₂ by weathering reactions, resulting in global cooling and increased continental ice buildup through the Cenozoic. This hypothesis is largely based on the rapid rate of increase in the strontium isotopic ratio of marine carbonates since 40 Ma, cited as evidence for an increase in the rate of radiogenic (continental) strontium input to the ocean. Although the uplift and weathering of the Himalayan-Tibetan Plateau must have had profound effects on global ocean biogeochemical cycles, especially considering the large drainage area and unique geochemical characteristics of this region (Raymo and Ruddiman 1992, Edmond 1992), some studies have called into question the direct link between Sr isotopic values and net chemical and sedimentological fluxes to the ocean (Rea 1992, Filippelli and Delaney 1994, Delaney and Filippelli 1994, Raymo 1994a, Kump and Arthur 1997). A shortcoming of many of these studies is the attempt to link one or several of these oceanic geochemical indicators to records of climate change and tectonics throughout the Cenozoic or a large portion of it.

The goal of this discussion is to trace the effect that the proposed intensification of the Asian monsoon at about 8 Ma had on continental weathering, geochemical and sedimentological fluxes to the ocean, biogeochemical cycles in the ocean, and the possible feedbacks to global climate (Filippelli 1997b). The Asian monsoon is a major climate system that currently affects global weather patterns. Massive warm rainfall events in late summer (from the Asian monsoon) combined with high elevations result in a disproportionate amount of chemical weathering occurring in the Himalayan-Tibetan Plateau; dissolved chemical fluxes in rivers draining this region account for about 25% of the global total, even though this region constitutes only slightly more than 4% of the global drainage area (Raymo and Ruddiman 1992). Oceanic and continental records suggest that the Asian monsoon may have intensified ~8 Myr ago (Kroon et al. 1991, Prell et al. 1992, Molnar et al. 1993), possibly as a result of an uplift event in the Himalayan-Tibetan Plateau (Prell and Kutzbach 1992). Several researchers have

highlighted the potential importance of this major climatic event on global cycles (Janecek and Rea 1983, France-Lanord and Derry 1994, Derry and France-Lanord 1996), and Piasias et al. (1995) called directly on increased chemical weathering rates in the Himalayan-Tibetan Plateau, in response to the Asian monsoon, as a cause for the “biogenic bloom” event documented recently in many ocean basins at this time.

Weathering changes in the Himalayan-Tibetan plateau

Several records of weathering changes in the Himalayan-Tibetan Plateau centering around 8 Ma have been extracted from the Indus and Bengal fans of the northern Indian Ocean. In a study of temporal trends in sediment flux rates to both the Indus and Bengal fans, Rea (1992) determined two main peaks in sediment input derived from the Himalayan-Tibetan Plateau. The largest of these peaks begins between 9 and 8 Ma and persists to about 5 Ma (Fig. 12). Sediments associated with this peak are clearly Himalayan in origin, and the sediment input spike is probably related to uplift and erosion of the Himalayan-Tibetan Plateau (Rea 1992). France-Lanord and Derry (1994) and Derry and France-Lanord (1996) presented clay mineralogy and grain-size data from the Bengal fan in the Indian Ocean indicating that chemical weathering intensity in the Ganges-Brahmaputra watersheds increased to a peak between 8 and 7 Ma. The increased chemical weathering intensity in material weathering from the Himalayan-Tibetan Plateau is likely to have resulted in large increases in dissolved material, due to the effective leaching of interlayer cations and oxyanions during clay formation and transformation processes (e.g., Birkeland 1984). Thus, it is plausible that an uplift event produced more physical weathering products and intensified the Asian monsoon, causing these weathering products to undergo intense chemical weathering. Recent evidence from ocean drilling in the western Atlantic Ocean indicates a similar uplift and weathering history for the Andes, with uplift causing orographic precipitation from trade winds and resulting in greatly increased sediment flux to the Atlantic at 8 Ma (Curry et al. 1995). Increased rainfall in the Amazon basin may have combined with the higher amount of weatherable material in increasing chemical weathering rates from this region. In order to explore the global effect of these regional phenomena, I will examine several key oceanic geochemical records.

Continental weathering and increased chemical fluxes to the ocean

Several records reveal increased rates of elemental input to the ocean beginning at about 8 Ma. The global decrease in the oceanic Ge/Si ratio of opaline diatoms over the past 35 Myr is interpreted to reflect increased rates of total weathering, particularly an increase in the rate of physical weathering versus chemical weathering (Shemesh et al. 1989). Superimposed on this overall decrease is a temporary reversal of this trend beginning at 8 Ma and reaching a peak at about 6 Ma (Fig. 12). This short-term increase, not discussed by Shemesh et al. (1989), whose focus was on the Cenozoic record, indicates a rapid increase in the proportion of chemical versus physical weathering. Using the mass-balance assumptions of Delaney and Filippelli (1994), the relative increase of 0.1 $\mu\text{mol/mol}$ in the oceanic Ge/Si ratio from about 9 to 6 Ma was caused either by up to a 27% increase in Ge river input (assuming constant Si river flux), a 14% lower Si river flux (assuming constant Ge/Si ratio of river input), or some combination of the two. Several lines of evidence suggest that, if anything, river fluxes of Si from the Himalayan-Tibetan Plateau increased during this interval. First, the peak in sediment input argues for a greater net surface area of eroded material from the Himalayan-Tibetan Plateau, and thus higher chemical leaching rates of Si. Second, the “biogenic bloom” event noted by Piasias et al. (1995) and Farrell et al. (1995a) occurs during this interval. Carbonate accumulation rates peak in many ocean basins during this interval (Pacific: Rea et al. 1995, Berger et al. 1993, Piasias et al. 1995, Farrell et al. 1995b, Indian: Peterson et al.

1992), and opal accumulation rates are also high (Leinen 1979, Kemp and Baldauf 1993, Farrell et al. 1995b, Rea et al. 1995, Rea and Snoeckx 1995). For all of these accumulation rate records, a net increase in global oceanic burial rate on these time scales is likely driven by an increase in the dissolved input of these elements from continental weathering. Thus, a marked increase in the Ge/Si ratio of river input beginning about 8 Ma is the most likely cause of the increase in oceanic Ge/Si ratios, and, using the arguments presented in Murnane and Stallard (1990), this increase was probably caused by a relative intensification of chemical weathering at this time.

Nutrient fluxes to the ocean

Given the role of P as a limiting nutrient in the ocean (Smith 1984, Codispoti 1989), geologic records of the accumulation rate of P in the ocean can be a window not only on P input rates from weathering but also on paleoproductivity (Filippelli and Delaney 1994, Delaney and Filippelli 1994, Föllmi 1995, Delaney 1998). The Neogene record of phosphorus accumulation rates in the equatorial Pacific reveals a large increase beginning at about 8 Ma and peaking by 6 Ma (Fig. 12). Through a series of mass-balance calculations, Filippelli and Delaney (1994) argued that this increase must reflect a net increase in the rate of phosphorus input to the ocean, and cannot be accounted for simply by changing the distribution of phosphorus within the ocean. Furthermore, other records from the Pacific (Moody et al. 1988), the western Atlantic (Delaney and Anderson 1997), and the Indian Oceans (Hermoyian and Owen 2000) reveal this increase in phosphorus accumulation rates. This phosphorus peak coincides with high rates of physical and chemical weathering likely deriving from the Himalayan-Tibetan Plateau (and possibly the Andes and Amazon Basin), as well as high biogenic productivity recorded in ocean sediments during this interval.

The mechanism for high phosphorus weathering rates during intense chemical weathering is revealed by a modern analog in the Amazon basin. In the lower Amazon, the transport-limited regime yields soil material that is nearly completely leached of phosphorus (Stallard and Edmond 1983), a nutrient limitation that requires ecosystems in this region to extensively recycle this element (e.g., Schlesinger 1997). Thus, an episode of high physical weathering rates in the Himalayan-Tibetan Plateau and other uplifting regions, coupled with high water fluxes and extensive chemical weathering in associated lowlands (Derry and France-Lanord 1996), would likely result in high phosphorus weathering rates and higher inputs of this nutrient to the ocean as reflected in the phosphorus accumulation rate trend.

The nutrient pulse to the ocean would be expected to increase net primary productivity and the export of organic carbon to the seafloor on these time scales. This hypothesis is supported by two observations. First, Dickens and Owen (1994) suggested that a broad expansion of the oxygen minima zone during this interval was caused by an increase in carbon export and oxidation at the sea floor, possibly driven by an increase in the net flux of nutrients to the ocean. Second, a transient positive excursion in the ocean-wide $\delta^{13}\text{C}$ of bulk carbonates coincides with the nutrient pulse (Fig. 12). The carbon isotopic composition of bulk carbonates is a function of the proportion of organic to inorganic carbon burial in the ocean, as well as the carbon isotopic values and fluxes of carbon to the ocean from rivers. The Neogene trend of more negative values toward the present has been interpreted as a decrease in the proportion of organic to inorganic carbon burial (Shackleton 1987). By analogy, the relatively short-term positive excursion beginning in the late Miocene may reflect a temporary increase in organic to inorganic carbon burial. Raymo (1994a), using the carbon isotope curve from Shackleton (1987, Fig. 12) and a strontium isotope mass balance, calculated a short-term maxima in organic carbon burial rates from 8 to 5 Ma, with rates 16% higher than preceding values. Another

approach, using the increase in reactive phosphorus input rates to the ocean suggested for this interval (Filippelli and Delaney 1994) and assuming that this increase directly drives organic matter burial, yields an increase in organic carbon burial of 20%. Thus, two different approaches result in similar magnitudes of organic carbon burial increases during the late Miocene to early Pliocene. At this point, however, changes in the isotopic composition of carbon input to the ocean cannot be ruled out (especially given evidence for major changes in C3/C4 vegetation assemblages in the late Miocene), which may themselves have been changed due to different rates of carbon weathering and/or intensification of chemical weathering at this time (e.g., Derry and France-Lanord 1996, Cerling et al. 1997, Pagani et al. 1999).

Late Miocene – early Pliocene weathering event and climate

A significant increase in the rate of chemical weathering during the late Miocene - early Pliocene may have had an impact on the long-term carbon cycle. First, the direct effect of the weathering of silicate minerals (combined with calcium carbonate sedimentation in the ocean) is an important long-term sink for atmospheric carbon (e.g., Berner et al. 1983). Second, an increase in organic matter production and burial in the ocean due to an increase in the nutrient flux is an additional sink for atmospheric carbon. Most models of Cenozoic climate invoke just such long-term carbon sinks for the observed deterioration of global climate (e.g., Raymo and Ruddiman 1992). Did the increased drawdown of atmospheric CO₂ inferred from the geochemical records presented here (Fig. 12) have any effect on climate trends in the Neogene? Hodell et al. (1989) linked higher chemical weathering rates in the late Miocene - early Pliocene to increased glaciation in Antarctica. The cause of the decrease in the rate of increase in the marine ⁸⁷Sr/⁸⁶Sr ratio during the interval between 6 and 4 Ma (Fig. 12) is unclear—in fact, Taylor et al. (2000) suggested that this flattening was due to a basalt-weathering event from the Columbia Plateau. Miller et al. (1987) suggested a possible ice growth event near the middle to late Miocene boundary. The oxygen isotope record from benthic foraminifera shows little change during the late Miocene to early Pliocene (Fig. 12). This record suggests a relatively stable climate (in terms of temperature and ice volume) during this interval until about 2.8 Ma, at which time extensive Northern Hemisphere glaciation commenced (e.g., Raymo 1994b and references therein), and the δ¹⁸O of the ocean increased. The continental weathering event appears to have had little immediate effect on climate, although a long-term drawdown of atmospheric CO₂ associated with this weathering event may have tipped the climate balance from its previous stable state (14 to 3 Ma) to the Pliocene - Pleistocene situation of lower temperatures and greater ice volume. It should be noted, however, that several important factors need to be considered related to this scenario. Recent work by Pagani et al. (1999) indicates little change of atmospheric CO₂ through the Miocene. Furthermore, Wells et al. (1999) suggested that the biogenic bloom observed in the Pacific was a result of increased loads of upwelled iron, derived from submarine volcanism related to the tectonic evolution of Papua New Guinea (in a process similar to upwelled iron in the Southern Ocean; Latimer and Filippelli 2001). Thus, the crystal ball of science is murkier than usual during this interval, and will only be cleared up by more work on productivity and weathering records.

CONCLUSIONS

Significant advances have been made in our understanding of the dynamics of the global P cycle. Interestingly, many of these advancements are derived from the widespread application of P geochemical techniques developed for soils and sediments over the last several decades, but only recently adopted by oceanographers. These techniques have allowed us to further elucidate the dynamics of P transformations during

weathering, transport, and deposition; the role that P bioavailability plays on terrestrial and marine ecosystems; and the impacts of P availability on biotic systems and climate change in the past. Despite these recent advances, several gaps exist in our knowledge of the global P cycle. I believe that several specific questions will drive research on the P cycle over the next decade.

What happens to P during transport from river mouths to sediments? Continental margins and marginal sediments play a significant role in the cycling of P, with about 50% of total P input to the ocean deposited in marginal sediments. Given this significance, we have only a few spotty records of P cycling on margins, and most focus on low oxygen settings. A more comprehensive examination of P sedimentation, sedimentary cycling, and eventual burial on continental margins is called for to address this lack of data. This effort should examine margins with large river inputs like the Mississippi, Amazon, and Ganges, together with smaller, more well constrained systems with a variety of sedimentation rates. Sampling should include coring and benthic flux chambers, which together would constrain sedimentation, cycling, and burial, placed along the margin and across the margin. Water column sampling and experimentation (e.g., Benitez-Nelson 2000) should be tied in with the core locations, involving sediment traps deployed over several years. Analytical methods could include P geochemistry, pore fluid analysis for the cores, isotopic analysis of organic matter (a critical component of the sedimentary P cycle) and sedimentology. This “source-to-sink” approach for P could be coupled to C and N to provide a clearer picture of nutrient and carbon cycling on continental margins. This approach would basically capture the anthropogenically modified P cycle, but could provide critical information about cycling across a wide range of systems on monthly, seasonal, and annual timescales. With this information, we could also hindcast the effects of changes in river input and more importantly the effects of changing sea level on continental margin P cycling.

How is the record of P accumulation in deep-sea sediments related to P input from land? As outlined here, a number of efforts have used records of P accumulation in deep-sea sediments to determine changes in P input to the ocean, and hence potential changes in marine productivity. But this “picture” of terrestrial P weathering is filtered through the dynamic continental margin system. Unfortunately, it is difficult to separate the terrestrial and marginal influences—for example, terrestrial P cycling clearly changed due to continental glaciation through the Pleistocene G/IG cycles, but so did sea level and thus marginal sedimentation. Perhaps the best way to answer this is to focus on several intervals with significant changes in sea level, but perhaps similar net climatic regimes. A comprehensive examination, for example, of deep sea P accumulation rates from the late Oligocene to the middle Miocene would allow one to examine the effects of significant second order changes in eustatic sea level (and thus changing deposition on the continental margins) on the oceanic P cycle in the face of more stable climatic conditions on land (compared to the rest of the Cenozoic, at least). This analysis would also be able to elucidate the true role of the deposition of the P-rich Miocene Monterey Formation on the oceanic P cycle. Adequate coverage of both high productivity and low productivity, above CCD and below CCD, and opal versus carbonate versus terrigenous sedimentation dominance would be required to truly close the deep sea P mass balance in such a study.

How did terrestrial P cycling change during the evolution of rootedness in land plants? Much has been said about, and debated on, the development of rootedness and its effects on soil development, chemical weathering, and climate during the Phanerozoic (e.g., Algeo et al 1995, Martin 1996, Berner 1997). A large gap exists, however, in determining the characteristics of soil development, weathering, and terrestrial nutrient

cycling during this time. One exciting but undeveloped aspect of this is an examination of P geochemistry of Phanerozoic paleosols (old soil horizons) versus nearby lacustrine or marginal basin sediments. Although diagenesis and rock-forming processes have likely altered the original composition, it might still be possible to extract a record of P cycling in paleosols in a similar manner as presented using lake sediment records earlier in this paper and outlined by Filippelli and Souch (1999). But to expand on this, one could apply geochemical proxies of weathering extent (e.g., Sr and Pb isotopes, Ti and Zr records) in conjunction with P geochemical analyses to examine whether the development of rootedness drastically altered the net chemical weathering and the release of nutrients from landscapes, thus permanently speeding up the soil development process and initiating a new and enhanced steady state for nutrients on land.

Although a few open and important research directions are noted above, it is likely that research on P and P-cycling will expand in a number of different and important ways over the next decade. These may include closing the biological production, recycling, sedimentation, and burial mass balances for P in a number of settings; improving the use of the oxygen isotopic composition of the phosphate molecule as a paleoproductivity proxy; improving our knowledge of the role of microbes in apatite weathering and determining soil-appropriate apatite weathering rate constants; clarifying the roles of P, N, and silica (Si) as limiting nutrients in different oceanic environments and on different timescales; and comparing the reliability of a variety of paleoproductivity proxies (e.g., P accumulation rates, P/Ti ratios, Ba accumulation rates, micropaleontological and biochemical proxies, and carbon and nitrogen isotopic records) in the same place and on the same temporal scales. As with all endeavors, however, it will be with a driving curiosity and sense of wonder that we will slowly unlock the mysteries wrapped around this deceptively simple but critically important element.

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