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Productivity records from the Southern Ocean and the equatorial Pacific Ocean: Testing the glacial Shelf-Nutrient Hypothesis

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Abstract

Quantifying variations in oceanic nutrient mass balances is central to understanding the links between biological productivity, carbon cycle variations, and climate. One challenge in mass balance determinations is in developing appropriate proxies and applying them in a number of oceanic settings on comparable time scales. On glacial timescales, it is important to separate nutrient variations driven by external processes (e.g., continental weathering, dust inputs) from those driven by internal processes (i.e. changing loci of upwelling, changes in nutrient inventories). Here, we compare several upwelling regions as a first-order analysis of phosphorus (P) inventory variations in the ocean. Sea-level variations should have a profound impact on the continental margin sink of this biolimiting nutrient on glacial timescales. New estimates for a shorter response time of P in the ocean suggest that variations in the P cycle play a role on marine biological productivity, and thus the carbon cycle, during glacial/interglacial intervals. Although this glacial transfer of nutrients from shelves to the deep sea was postulated over two decades ago, few quantitative data have been produced to support or refute this hypothesis. Supported by a more thorough understanding of P sedimentary geochemistry, we present here detailed records of variations in oceanic P cycling on glacial timescales, showing that the redistribution of this nutrient from marginal to deep-sea sinks during glacial lowstands has had an impact on the oceanic P cycle. Furthermore, P-based records of export production from the Southern and equatorial Pacific oceans indicate that this redistribution of P resulted in higher oceanic dissolved P concentrations and increased oceanic productivity toward the end of glacials and the beginning of subsequent interglacials. A 10–20-kyr lag between P-based export production records and sea level supports the newer estimates of the marine P response time and indicates that this "nutrient lag" may be a heretofore unrecognized driver of other biological paleoproductivity records.

Keywords: Nutrients; Phosphorus Cycle; Carbon Cycle; Glacial-interglacial; Sea level

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1. Introduction

The impacts of sea-level variations on the storage of material on continental shelves have been examined from many perspectives. The gain and loss of a sedimentary sink that is small in area but large in terms of net accumulation and biogeochemical dynamics certainly plays a role in whole-ocean geochemical budgets. The Shelf-Nutrient Hypothesis (Broecker, 1982; Berger and Kier, 1984; Bertrand et al., 1996; Pollock, 1997) suggests that the loss in continental margin sinks for nutrients and carbon during glacial sea-level lowstands (which resulted in a Last Glacial Maximum decrease in continental margin area of 60% compared to now; Menard and Smith, 1966) should result in a net transfer of these components to the deep-ocean sink, the consequence being significantly different and climatically mediated deep-ocean budgets and biogeochemical responses for these elements. Many aspects of the Shelf-Nutrient Hypothesis have been tested and debated, most prolifically those related to carbon transfers (Hodell et al., 2001). Nutrient budgets also have been examined in the form of phosphate concentrations and inventories in the ocean using a variety of geochemical tracers in foraminifera (e.g., Cd/Ca; Ba/Ca; Lea and Boyle, 1990; Rickaby and Elderfield, 1999), and have shed some light on paleophosphate concentrations, but not on deep-ocean phosphorus (P) budgets. This is a particularly critical issue, given the role that P plays as a limiting nutrient (Tyrell, 1999; Wu et al., 2000; Sañudo-Wilhelmy et al., 2001; Ammerman et al., 2003) and, indeed, perhaps as the ultimate limiter of oceanic productivity on geologic timescales (Tyrell, 1999). Furthermore, the variability of P sedimentation on glacial timescales (Ganeshram et al., 2002) and its potential to both bypass the active margin sink and be weathered from marginal sediments—both these processes acting to increase the deep-ocean P reservoir—acts to increase glacial productivity in upwelling regions.

The evidence for and implications of the shift of nutrients from continental margins to the deep oceans has not been adequately examined in the past—this omission can be traced to several uncertainties in the P budget that have now been clarified. First, newer estimates of the P residence time, based on a more thorough understanding of P deposition and regeneration, center around 20 kyr (Ruttenberg, 1993; Filippelli and Delaney, 1996; Delaney, 1998; Colman and Holland, 2000; Anderson et al., 2001). This is a fundamental change in our understanding, indicating that the mass balance of P is responsive on glacial timescales. Second, we now recognize that although most dissolved biologically active P in the ocean is ultimately delivered to the seafloor as organically-bound and oxide-bound phases, it is relatively rapidly transformed by authigenesis into mineralized forms (predominantly carbonate fluorapatite—CFA; Ruttenberg and Berner, 1993; Filippelli and Delaney, 1996; Filippelli, 2001), which are resistant to further change in the ocean environment. Third, the accumulation rates of biologically reactive P are much more constrained, indicating that despite comprising less than 10% of total ocean area, the continental margin sink for P is almost equal to the deep-ocean sink because of high sedimentation rates, lower recycling, and relatively high marginal productivity (Fig. 1; Föllmi, 1996; Filippelli, 1997). Fourth, it is plausible to expect that material previously deposited on continental margins will now be exposed to subaereal weathering during glacial lowstands; this is important because the CFA, which comprises the bulk of the reactive P in continental margin sediments, is readily soluble in the weakly acidic conditions of subaereal exposure and weathering (Guidry and Mackenzie, 2003). Finally, the first measurements of P export from the continents to the ocean on glacial timescales indicate high rates of P weathering and transfer during glacial intervals, particularly at glacial terminations, and relatively lower export during interglacial intervals (Filippelli and Souch, 1999), thus, the net increase in P delivered to the deep ocean during glacials would include not only that transferred from the margin sinks but potentially that derived from increased continental input.

Together, these new developments support the potential impact that the loss of a continental margin sink has on oceanic P cycling, and indicate that this loss should be observable in deep-ocean records. We have found evidence for this profound change in the mass balance of P in geochemical records from two widely spaced areas of divergence: the southeastern Atlantic sector of the Southern Ocean and the eastern central equatorial Pacific. By linking Southern Ocean and equatorial upwelling zones using similar proxies and temporal ranges, we are working one step closer to ‘‘synthesizing’’ ocean biogeochemical records and integrating the Southern Ocean into a whole-ocean context. Combined,

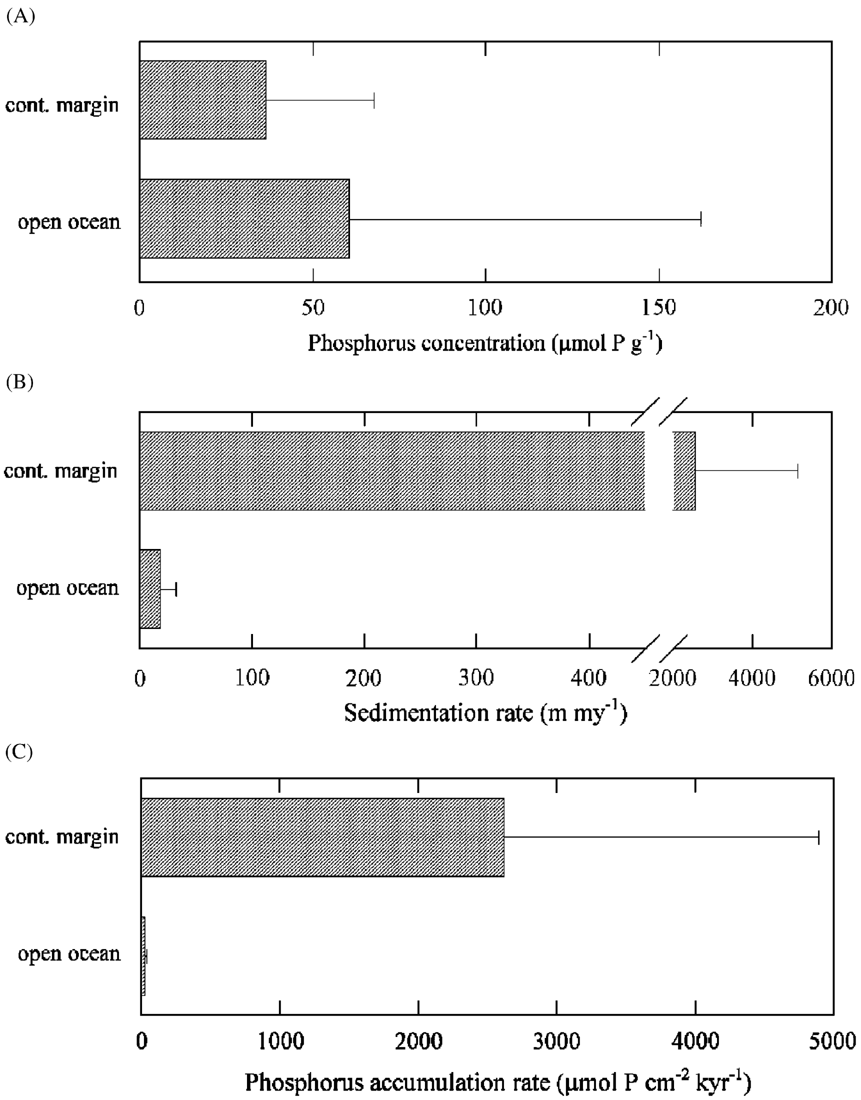

Fig. 1. A comparison of (A) P concentration, (B) bulk sedimentation rate, and (C) P accumulation rate for open-ocean and continental margin settings (revised from Filippelli, 1997). Note the importance of sedimentation rate along continental margins in driving high P accumulation rates.

these two areas alone represent the majority of the global budget of export production (Chavez and Barber, 1987; Arrigo et al., 1998), and thus provide an unparalleled opportunity to examine the potential linkages between climate, the input of nutrients to the deep sea, and the sequestering of these nutrients on a somewhat global basis.

2. Study site and methods

To assess the temporal record of P sedimentation at these sites, we determined the phosphorus/titanium (P/Ti) ratio at several deep-sea sites from the equatorial Pacific (Core TT013-PC72; 4298 m water depth, 0.1°N, 139.4°W, and Core TT013-PC114; 4432 m water depth, 4°N, 139.9°W) and Southern Oceans (ODP Site 1089; 4620 m water depth, 41°S, 10°E, and ODP Site 1094; 2807 m water depth, 53°S, 5°E) (Murray et al., 2000; Latimer and Filippelli, 2001a). In addition, we examined the record of biological productivity as reflected by the nannofossil accumulation rate at one Southern Ocean site. These proxies provide somewhat independent records and thus increase our confidence that our interpretations are not based on an approach that is method-dependent. The P/Ti ratio reflects "excess" P delivery to the seafloor not supported by terrigenous components. Thus, increases in the P/Ti ratio record higher P sedimentation to the seafloor from biological processes. Although not directly correlative to the P mass balance, this ratio limits the effect that sediment focusing has on biasing accumulation rate records in drift settings (Latimer and Filippelli, 2001b), yet retains the character of reflecting high biological export production. Temporal records can be affected somewhat by changes in the ratio of P to Ti in the terrigenous component alone; this does not appear to be an issue for the records presented here as they exhibit the same character when normalized to other terrigenous elements (e.g., Al[26]). The nannofossil accumulation rate record at Southern Ocean Site 1089 is a more integrated reflection of surface-water productivity than is the highly variable opal accumulation rate, and has proven to be a robust proxy for net surface-water production (Flores et al., 2003).

Southern Ocean Site 1089, recovered during Ocean Drilling Program Leg 177, is located within the present-day Subantarctic Zone, south of the Subtropical Front. The drilling site itself is located in the southern Cape Basin. Pleistocene sediments at this site are dominated by interbedded carbonate and opal oozes, and display a Pacific Pleistocene sedimentation pattern with glacial intervals marked by high carbonate content (Hodell et al., 2001). The central equatorial Pacific piston cores were gathered as part of the Joint Global Ocean Flux Study program (Murray et al., 2000). We selected two representative cores, Core TT013-PC72 and Core TT013-PC114, with particularly well-defined age models and sample resolution (Murray et al., 2000). Samples were analyzed by ICP-ES, and the procedures and data may be found in (Murray et al., 2000).

Geochemical analysis of ODP Site 1089 samples were performed by inductively coupled plasma-atomic emission spectrometry (ICP–AES) after complete digestion using a CEM Corp. MDS 2000 microwave digestion system, concentrated trace-metal grade acids, and following Environmental Protection Agency SW846 Method 3052. Once the digestion was complete, 0.1 g of boric acid was added to stabilize the solutions. Samples were transferred to new 50-ml polyethylene centrifuge tubes and diluted to 50 ml with Milli-Q water. A Leeman Labs P950 ICP-AES with a CETAC Corp. AT 5000+ ultrasonic nebulizer was used to determine the total elemental concentrations. Ten percent of the samples were analyzed as randomly chosen replicates, which agreed within 7% for all elements analyzed. Typical combined instrumental and replicate error for P at Site 1089 is small compared to the P concentration signal (Fig. 2); the combined errors for the metal concentrations are significantly smaller than for P. The precision of ratios was calculated and averaged 2% for the P/metal ratios. We normalized P both to Ti and to aluminum, and found nearly identical temporal trends (Latimer and Filippelli, 2001a)—we present

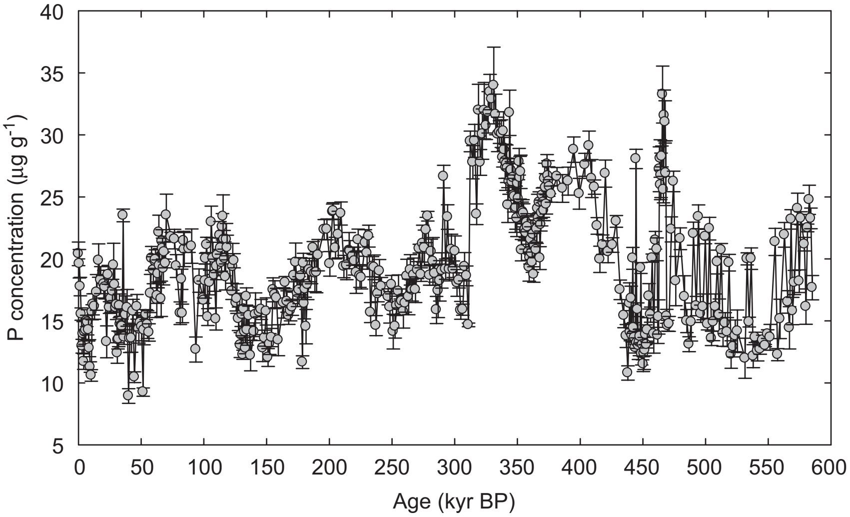

Fig. 2. Phosphorus concentrations and standard deviations for ODP Site 1089. These relative errors are typical of all phosphorus concentration determinations in this study.

P/Ti here to avoid issues of aluminum scavenging in opal during high productivity events (Murray et al., 1993; Murray and Leinen, 1996). Sedimentation rates were calculated from the revised age models of Hodell et al. (2001).

3. Results and discussion

The P/Ti records for these widely spaced sites show similarity over the last 400 kyr (Fig. 3). The source of terrigenous material to the seafloor is completely different in the southeastern Atlantic compared to the eastern equatorial Pacific, yet the absolute P/Ti ratio is nearly identical, exhibiting peak values between 0.3 and 0.6 and low values between 0.1 and 0.25 (Fig. 3). From 400 kyr to about 60 kyr ago, the absolute values, trends, and timing of P/Ti variations in these two sites match well. From about 60 kyr to present the records exhibit similar timing of peaks (with a notable exception at 10 kyr ago), but absolute values diverge somewhat. The P/Ti ratios at both sites exhibit a phasing of broad peaks that begins during glacial intervals, reaching maxima just after the glacial–interglacial transition, and then decrease to low values by the beginning of the next glacial interval. These records indicate relatively high "excess" P export occurring about 40–60 kyr after the onset of glacial intervals. Carbonate can be a significant carrier of P in marine sediments (Filippelli and Delaney, 1996) and in fact somewhat of a correlation exists between Ca and P/Ti in the southeastern Atlantic site for which we have adequate carbonate data ($r^2 = 0.51$). Nevertheless, about half of the variance still is not explained by carbonate alone. Furthermore, to test the role of sedimentology on the

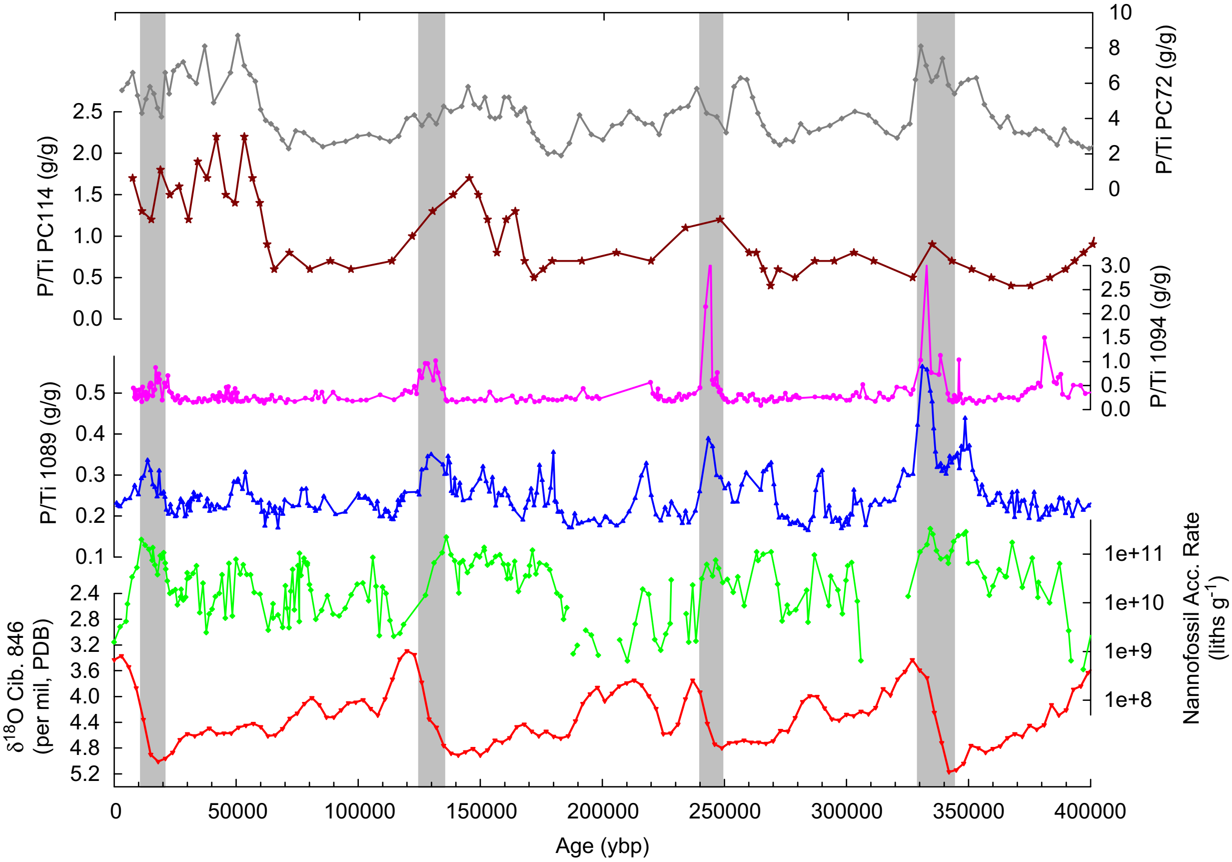

Fig. 3. Phosphorus/titanium ratios from four deep-sea sites (ODP Sites 1089 and 1094 in the southeastern Atlantic sector of the Southern Ocean, and JGOFS Cores PC 72 and PC 114 in the equatorial Pacific), nannofossil accumulation rates from ODP Site 1089, and oxygen isotope stratigraphy from ODP Site 846. Vertical gray bars represent glacial terminations. The P/Ti ratios reflect excess P export from the surface ocean related to surface productivity, revealing some coherent patterns of higher export of P during the latter stages of glacial intervals and the beginning of subsequent interglacials. This productivity pattern is also seen in the nannofossil accumulation rate record from the Southern Ocean site.

P/Ti we also examined P/Ti records of a site from ODP Leg 177 further to the south (Site 1094; Fig. 3) which exhibits an opposite sedimentological pattern from 1089 on glacial/interglacial timescales (in this case, the typical Atlantic pattern of opal in glacials and carbonate in interglacials). This site is completely ice covered during full glacial times, but upon deglaciation it also shows high P/Ti at the beginning of interglacials followed by a rapid decrease. The fact that these records, from disparate locations and with differing lithologies, site water depths, and sedimentation rates, exhibit similar records argues very strongly against sediment focusing as a prime control on the temporal records presented here.

We also determined nannofossil accumulation rates at ODP Site 1089 in the southeastern Atlantic Ocean (Fig. 3). Today this is a mesotrophic area with a moderate primary production, where coccolithophores play an important role, with their abundance linked to nutrient availability (Flores et al., 2003). For the interval investigated in ODP Site 1089, calcareous nannofossils are the dominant component of the carbonate fraction (Flores et al., 2003). The highest nannofossil accumulation and the highest calcium carbonate content occurred towards glacial periods and terminations, whereas minimum values are recorded in interglacial stages (Fig. 3). Although dissolution plays a role in the carbonate record during terminations (Hodell et al., 2001), an analysis of the total abundance of coccoliths versus the carbonate indicates that the longer-term record is related to the production of coccolithophores. The coccolith record of productivity based on accumulation rates coincides well with the P/Ti record of excess P export (and hence productivity), with higher values during glacials and lower values during interglacials.

The P accumulation rate record reflects the net mass of P permanently removed from the oceanic reservoir through time, and thus directly records variation in the P mass balance. Weaknesses inherent to P accumulation rate records are that they are site-specific, and thus unlike an isotope record, requires a number of sites in a wide range of oceanic settings to provide global constraints, that it depends strongly on the sedimentation rate, a notoriously under-constrained variable in paleoceanographic studies, and that it is potentially influenced by sediment focusing and/or sediment winnowing. For the purposes of the results presented here, the P accumulation rate records are illustrative of variations in P sedimentation in several widely spaced sites on glacial timescales—thus some of the weaknesses are controlled and models presented are calculated on a relative (fractional) scale, with the deep-sea P accumulation rate records compared to estimated percent relative increases expressed as a function of the loss of continental margin sinks on a percentage basis.

Phosphorus accumulation rate records exhibit a wide range in absolute values at the various sites, but coincide in timing and direction (Fig. 4). For example, the southeastern Atlantic Ocean site has extremely high P accumulation rates (up to nearly 1300 μmol cm^{-2} kyr^{-1}) compared to the deep-ocean average of about 40 μmol cm^{-2} kyr^{-1} (Fig. 1; Filippelli, 1997); those in the eastern equatorial Pacific sites are close to average (Fig. 4). This difference in accumulation rates is partly ascribable to the high sedimentation rates and high terrigenously associated P seen in the southeastern Atlantic site (Latimer and Filippelli, 2001b); nevertheless, much of this P burial is in fact reactive P, and thus, although the Southern Ocean is areally small, it is still an important sink in the marine P mass balance. Perhaps the most intriguing aspect of these comparative records is their timing. Records from both settings reveal sharp peaks 40–60 kyr after glacial onset, followed by a slow decline, with some abbreviated peaks, over the ensuing 60–80 kyr (Fig. 4). The timing of the records from the southeastern Atlantic and the eastern equatorial Pacific are not as similar as for the P/Ti records, with peaks in the Pacific lagging those in the Atlantic. This lag is driven by sedimentation rate differences between the Atlantic and Pacific sites. The isotopic stratigraphy is equivalent, and thus age assignments are robust, but the peak in bulk sedimentation is delayed by about 20–30 kyr in the Pacific compared to the Atlantic site. The nature of the records, however, is similar in both settings, and thus it is appropriate to examine what mechanisms might be driving these observed changes in the marine P mass balance.

These semi-independent proxies provide a picture of a potentially globally coherent signal in the deep-ocean marine P mass balance. This point is critical, in that the sites examined reside in oceanographic provinces responsible for more than 90% of deep-ocean new production and thus are important indicators of variations in the biological pump. Both P/Ti ratios and P accumulation rates point to high rates of biologically cycled P burial approximately 40–60 kyr after the onset of glacial intervals,

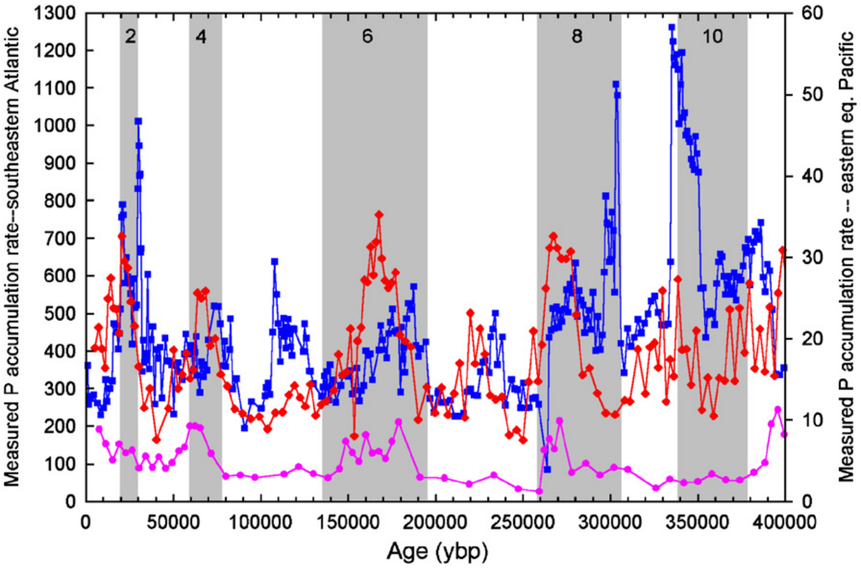

Fig. 4. Phosphorus accumulation rates through time (in units of μmol cm^{-2} kyr^{-1}); blue squares are from ODP Site 1089 in the southeastern Atlantic Ocean (left scale), and red and purple diamonds are from the equatorial Pacific Ocean (JGOFS sites PC72 and PC114, respectively; right scale).

followed by a slow decline in the succeeding 60–80 kyr. Several mechanisms, including enhanced upwelling and iron fertilization, could be invoked to partly explain the timing and magnitude of these records as they relate to surface ocean productivity processes. Although important for understanding the interplay between nutrient dynamics, total productivity, export production, and climate, these hypotheses do not address an equally important question: might variations in the fractionation of burial sinks for P on glacial/interglacial timescales drive these records?

The redistribution of P from continental margins to the deep-sea during glacial lowstands, and the subsequent deep-sea response to this increased P loading, can be simplistically modeled to a first-order by using the sea-level curve to estimate continental margin sink loss. A simple but illustrative exercise involves examining several delay intervals between sea-level state and the net impact on nutrient mass balances. The premise here is that the transfer of nutrients from the continental shelf sink will start immediately upon a sea-level drop associated with glaciation, but the net impact on the P deep-sea mass balance will be delayed in accordance with the oceanic response time of P (current estimates for the P residence time in the ocean are 10–20 kyr; Ruttenberg, 1993; Filippelli and Delaney, 1996; Colman and Holland, 2000). The inherent assumption here is that P burial is controlled only by internal reorganization of burial sinks within the mass balance. This assumption is not likely quantitatively robust given the potential for changes in terrigenous weathering and input of P (e.g., Filippelli and Souch, 1999), but as noted previously this would have a temporal pattern similar to that of the model assumption, and thus likely have an additive effect.

In this model exercise, sea-level variation is derived from the composite oxygen isotopic record from ODP Site 846 in the eastern equatorial Pacific (a global reference site; Raymo et al., 2004). The inverse of the sea-level curve is used to predict the shift of nutrients from the continental margin to the deep-sea sink. Two response time lags are used to bracket the estimates of the P residence time (10 and 20 kyr). The obvious result is that P should increase in the deep-sea sink after sea-level lowstands related to glacial onset. To examine whether this delayed nutrient redistribution appears in the deep sea, we developed composite records for P/Ti from all sites except the Southern Ocean site significantly impacted by permanent ice cover (ODP Site 1094).

The values for P/Ti were averaged in 10-kyr bins for each of three sites (Site 1089 in the Southern Ocean and PC72 and PC114 in the equatorial Pacific), normalized to enrichment factor over baseline at each site, and then averaged across all three sites (the normalization to enrichment factor controlled for varying baseline and maximum values at each site). The temporal record of these sites reveals generally low interglacial values and high glacial and termination values (Fig. 5), with the scale of variation reaching 2.8 times baseline values just after glacial terminations. This result is consistent with the individual records (Fig. 3). The deep-sea nutrient model provides an extremely good fit to the composite P/Ti record with a 20-kyr lag (a 10-kyr lag is also shown). Two remarkable aspects of these comparative records emerge from this analysis. First, even a simple comparison of excess P export from these three sites results in a reasonable fit to a deep sea nutrient model based on global sea-level variations alone. Second, the 20-kyr lag that provides the best long-term fit to the P/Ti data is what would be expected given the P response time in the ocean as currently estimated (between 10 and 20 kyr). Interestingly, given the decay curve response expected by mass balance constraints (86% of total response after 2 × the residence time of the component), the comparison of the P/Ti and nutrient model curves argues for a response time of P closer to 10 kyr in this dynamic mass balance.

Of course, there are many shortcomings with this approach. For example, response times in mass balances are dynamic, and multiple perturbations to inputs or outputs on timescales within several multiples of a response time will yield a more complicated temporal record that can be achieved with this simplistic model. In addition, the P/Ti composite record may be driven by coincidental long-term trends in export production alone. If reflecting productivity variations in export flux, they must be related to processes occurring in both the southeastern Atlantic and the eastern equatorial Pacific, including among other possibilities, enhanced upwelling and/or higher rates of upwelled (Latimer and Filippelli, 2001b) or dust-delivered iron. P/Ti exhibits a 2-fold increases in late glacial/termination intervals, with a relatively consistent pattern over the past 400 kyr. In a simple mass balance model for P based on internal reorganization, the total deep-sea reactive P burial would increase by about 2 × globally based on shelf versus deep-sea sinks (Filippelli and Delaney, 1996), resulting in an average site-specific increase in P accumulation rates of about 2 × as well. Given that high productivity settings are responsibility for the majority of reactive P accumulation, it is quite feasible that these areas would have much higher net P accumulation rate increases in response to the transfer of nutrients to the deep-sea sink than would red clay provinces, for example, and thus it is reasonable to see a net increase in P/Ti ratio on the order of 2–5 × as seen here (Fig. 3). Because the equatorial Pacific and the Southern Ocean collectively account for the majority of oceanic new production at present, the global significance of the observed glacial/interglacial variations in P/Ti cannot be overstated. Altogether, the excellent temporal correlation between the observed deep-sea nutrient

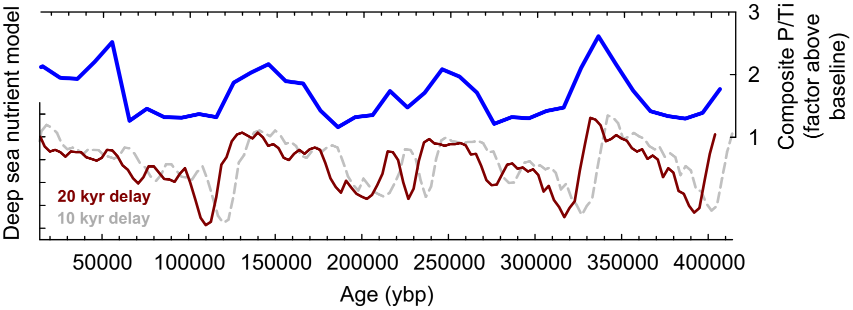

Fig. 5. Composite P/Ti record using binned averages (10 kyr) of equatorial Pacific and southeast Atlantic sites (ODP Site 1089 in the southeastern Atlantic sector of the Southern Ocean and JGOFS Cores PC 72 and PC 114 in the equatorial Pacific), versus modeled response of deep sea nutrient budgets to changes in marginal sink using two residence time parameters: 10 kyr (gray line) and 20 kyr (brown line). P/Ti values are normalized to enrichment factor over baseline at each site, and then averaged across all three sites (the normalization to enrichment factor controlled for varying baseline and maximum values at each site). The deep-sea nutrient model is simply the sea-level record interpretation of the oxygen isotopic record for ODP Site 846; considered to be a relatively robust and continuous whole-ocean record. Note the quantitative transfer of nutrients from continental margins recorded by the P/Ti record is best matched by the nutrient model with a 20-kyr lag; thus the net impact of redistribution of marginal nutrients to the deep sea matches with the predictions of the P response time in the ocean.

excess record and the deep-sea nutrient model driven by a variable continental margin sinks indicates that on a first order, this model is relatively successful.

4. Implications

The shifts in the oceanic P mass balance supported by these deep-ocean records have several important implications for global ocean productivity variations and carbon cycling. First, changing the depositional sink of P from high sedimentation rate/short water-column continental margins to low sedimentation rate, deep-ocean basins would enhance the degree of recycling of P from particulates to dissolved phase both in the water column and at the sediment–water interface. Thus, the oceanic dissolved P inventory should increase in response to the glacial loss of a marginal P sink. Is this seen in other proxy records? The Cd/Ca records show little indication of higher glacial values related to phosphate concentrations in the deep sea (Rickaby and Elderfield, 1999), but it should be noted that the mass balances of Cd and P are independent, and, for example, the slope of the Cd/P relationship could vary over time. Whereas the temporal record of Cd/Ca in the deep sea is an excellent tool for reconstructing paleo-phosphate concentration gradients, it is not particularly useful for reconstructing the P mass balance. Second, if the phosphate inventory is in fact increased during and just after glacials, observed increases in surface water productivity would not necessarily be the result solely of increased wind-driven upwelling, but perhaps could be caused by the same rate of water upwelling, but with an increased preformed phosphate concentration. Both Southern Ocean and equatorial Pacific δ^{13}C records exhibit negative excursions near terminations; this has largely been interpreted as changes in ventilation and/or deep-water circulation (Oppo et al., 1990; Spero and Lea, 2002). However, it is possible that some portion of this δ^{13}C minimum reflects nutrient increases that led to increased P burial due to increased primary productivity and export production. Additional work to examine the implications of this hypothesis should include an assessment of changes in the C:P ratio on glacial timescales as well as more detailed modeling of the sea-level curve and its effects on shelf-deep-sea fractionation. Nonetheless, at this initial stage the paleoceanographic records of P records presented do provide deep-sea support for the "Shelf-Nutrient Hypothesis," and should spur continued examination of geochemical mass balance variations through time.

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References

Ammerman, J.S., Hood, R.R., Case, D.A., Cotner, J.B., 2003. Phosphorus deficiency in the Atlantic; an emerging paradigm on oceanography. Eos 84, 165.

Anderson, L.D., Delaney, M.L., Faul, K.L., 2001. Carbon to phosphorus ratios in sediments: implications for nutrient cycling. Global Biogeochemical Cycles 15, 65–79.

Arrigo, K., Worthon, D., Schnell, A., Lizotte, M.P., 1998. Primary production in Southern Ocean waters. Journal of Geophysics Research 103, 15587–15600.

Berger, W.H., Kier, R.S., 1984. Glacial-Holocene changes in atmospheric CO_2 and the deep-sea record, climate processes and climate sensitivity. Geophysical Monograph 29, 337–351.

Bertrand, P., and 14 others, 1996. The glacial ocean productivity hypothesis: the importance of regional temporal and spatial studies. Marine Geology 130, 1–9.

Broecker, W.S., 1982. Glacial to interglacial changes in ocean chemistry. Progress in Oceanography 11, 151–197.

Chavez, F.P., Barber, R.T., 1987. An estimate of new production in the equatorial Pacific. Deep Sea Research 34, 1229–1243.

Colman, A.S., Holland, H.D., 2000. The global diagenetic flux of phosphorus from marine sediments to the oceans; redox sensitivity and the control of atmospheric oxygen levels. Special Publication–Society for Sedimentary Geology, vol. 66, pp. 53–75.

Delaney, M.L., 1998. Phosphorus accumulation in marine sediments and the oceanic phosphorus cycle. Global Biogeochemical Cycles 12, 563–572.

Filippelli, G.M., 1997. Controls on phosphorus concentration and accumulation in oceanic sediments. Marine Geology 139, 231–240.

Filippelli, G.M., 2001. Carbon and phosphorus cycling in anoxic sediments of the Saanich Inlet, British Columbia. Marine Geology 174, 307–321.

Filippelli, G.M., Delaney, M.L., 1996. Phosphorus geochemistry of equatorial Pacific sediments. Geochimica et Cosmochimica Acta 60, 1479–1495.

Filippelli, G.M., Souch, C., 1999. Effects of climate and landscape development on the terrestrial phosphorus cycle. Geology 27, 171–174.

Flores, J-A., Marino, M., Sierro, F.J., Hodell, D.A., Charles, C.D., 2003. Calcareous plankton dissolution pattern and coccolithophore assemblages during the last 600-kyr at ODP Site 1089 (Cape Basin, South Atlantic): Paleoceanographic implications. Palaeogeography, Palaeoclimatology, Palaeoecology 196, 409–426.

Föllmi, K.B., 1996. The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits. Earth Science Reviews 40, 55–124.

Ganeshram, R.S., Pedersen, T.F., Calvert, S.E., Francois, R., 2002. Reduced nitrogen fixation in the glacial ocean inferred from changes in marine nitrogen and phosphorus inventories. Nature 415, 156–160.

Guidry, M.W., Mackenzie, F.T., 2003. Experimental study of igneous and sedimentary apatite dissolution: control of pH, distance from equilibrium, and temperature on dissolution rates. Geochimica et Cosmochimica Acta 67, 2949–2963.

Hodell, D.A., Charles, C.D., Sierro, F.J., 2001. Late Pleistocene evolution of the ocean's carbonate system. Earth and Planetory Science Letters 192, 109–124.

Latimer, J.C., Filippelli, G.M., 2001a. Data report. Sediment Geochemistry at Site 1089. In: Gersonde, R., Hodell, D., Blum, P. et al. (Eds.), Proceedings Ocean Drilling Program, Scientific Results, vol. 177, pp. 1–14.

Latimer, J.C., Filippelli, G.M., 2001b. Terrigenous input and paleoproductivity in the Southern Ocean. Paleoceanography 16, 627–643.

Lea, D.W., Boyle, E.A., 1990. Foraminiferal reconstructions of barium distributions in water masses of the glacial oceans. Paleoceanography 5, 719–742.

Murray, R.W., Leinen, M., Isern, R.A., 1993. Biogenic flux of Al to sediment in the equatorial Pacific Ocean; evidence for increased productivity during glacial episode. Paleoceanography 8, 651–670.

Menard, H.W., Smith, S.M., 1966. Hypsometry of ocean basin provinces. J. Geophys. Res. 71, 4305–4325.

Murray, R.W., Leinen, M., 1996. Scavenged excess Al and its relationship to bulk Ti in biogenic sediment from the central equatorial Pacific Ocean. Geochimica et Cosmochimica Acta 60, 3869–3878.

Murray, R.W., Knowlton, C., Leinen, M., Mix, A., 2000. Export production and carbonate dissolution in the central equatorial Pacific Ocean over the past 1 Ma. Paleoceanography 15, 570–592.

Oppo, D.W., Fairbanks, R.G., Gordon, A.L., Shackleton, N.J., 1990. Late Pleistocene Southern Ocean $\delta^{13}C$ variability. Paleoceanography 5, 43–54.

Pollock, D.E., 1997. The role of diatoms, dissolved silicate and Antarctic glaciation in glacial/interglacial climatic change; a hypothesis. Global and Planetary Change 14, 113–125.

Raymo, M.E., Oppo, D.W., Flower, B.P., Hodell, D.A., McManus, J., Venz, K.A., Kleiven, K.F., McIntyre, K., 2004. Stability of North Atlantic water masses in face of pronounced climate variability during the Pleistocene. Paleoceanography 19, 2008–2021.

Rickaby, R.E.M., Elderfield, H., 1999. Planktonic foraminiferal Cd/Ca: paleonutrients or paleotemperature? Paleoceanography 14, 293–303.

Ruttenberg, K.C., 1993. Reassessment of the oceanic residence time of phosphorus. Chemical Geology 107, 405–409.

Ruttenberg, K.C., Berner, R.A., 1993. Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. Geochimica et Cosmochimica Acta 57, 991–1007.

Sañudo-Wilhelmy, S.A., Kustka, A.B., Gobler, C.J., Hutchins, D.A., Yang, M., Lwiza, K., Burns, J., Capone, D.G., Raven, J.A., Carpenter, E.J., 2001. Phosphorus limitation of nitrogen fixation by *Trichodesmium* in central Atlantic Ocean. Nature 411, 66–69.

Spero, H.J., Lea, D.W., 2002. The cause of the carbon isotope minimum event on glacial terminations. Science 296, 522–525.

Tyrell, T., 1999. The relative influence of nitrogen and phosphorus on oceanic primary production. Nature 400, 525–527.

Wu, J., Sunda, W., Boyle, E.A., Karl, D.S., 2000. Phosphate depletion in the western North Atlantic Ocean. Science 289, 759–762.