Opal-associated particulate phosphorus: Implications for the marine P cycle

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Abstract

Previous attempts to evaluate ocean P mass balance and residence time have utilized sequential extraction techniques to isolate and analyze P associated with Fe and Mn oxides and oxyhydroxides, authigenic minerals, detrital, and organic phases. However, in many oceanographic settings, diatoms are the primary producers, and the traditional sequential extraction protocol does not result in complete dissolution of diatom frustules and may not liberate all of the opal intrinsic P associated with the frustules themselves. By adding an opal dissolution step to the end of the extraction protocol, additional P was liberated from the sediments, suggesting that there is an opal-associated P fraction that likely contributes to total reactive P concentrations. In opal-rich sediments, the opal-associated P fraction averages as much as 50–60% of extractable P, and total reactive P concentrations are often more than double when the opal-associated P fraction is included. The presence of opal-intrinsic P potentially has significant implications for ocean P mass balance and residence time of P in the oceans. For example, P burial has possibly been underestimated in settings dominated by diatoms. Additionally, consideration of a significant sedimentary opal-P component suggests that the residence time of P in the oceans may be even shorter than currently suspected.

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1. Introduction

Because phosphorus (P) is an important nutrient element in the oceans, there is considerable interest in P biogeochemistry and burial fluxes to understand nutrient utilization and export production. The addition of new P to the oceans is controlled by the weathering of minerals, such as apatite, on land and subsequent delivery to the oceans via rivers. Because nitrogen has a vast atmospheric source compared to sources of new P to the ocean, P likely limits biological productivity on geologic time scales (Tyrrell, 1999). The importance of P limitation in the modern ocean has also been highlighted recently in the north Atlantic (Sañudo-Wilhelmy et al., 2001) and north Pacific (Karl et al., 2001). P is important biologically because it is involved in energy transfer reactions (ATP and ADP) and is a component of cell walls (phospholipids). In the open ocean, it is commonly believed that much of the P reaching the seafloor is associated with organic C, thus linking sedimentary P burial to overlying surface ocean productivity, although Paytan et al. (2003) have demonstrated that P undergoes significant reorganization in the water column from organic forms to inorganic forms. While P reaching the seafloor may no longer be technically associated with organic matter, it was likely once involved in biological reactions.

Sequential extraction techniques have been utilized to try to understand the diagenetic transformations of organic P in sediments, usually using some variation of the SEDEX reaction scheme (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1996; Slomp et al., 1998; Anderson and Delaney, 2000; Latimer and Filippelli, 2001; Slomp et al., 2002; Tamburini et al., 2002; van der Zee et al., 2002; Faul et al.,

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2003; FilippelliI et al., 2003). During diagenesis, organic P is released to pore waters where it can undergo several different chemical or physical processes including becoming associated with Fe and Mn oxides or oxyhydroxides, adsorbed to mineral surfaces, refluxed to the overlying bottom water, or converted to an authigenic mineral phase such as carbonate fluorapatite (CFA) (Ruttenberg, 1992). As a result of this diagenetic reorganization of P within sediments, organic P concentrations usually decrease with time as it is ultimately transformed to authigenic P during diagenesis (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1996; Delaney and Anderson, 1997; Anderson et al., 2001). Because CFA is relatively stable in ocean sediments, this systematic redistribution of P in sediments or "sink-switching" results in CFA being a long term net sink for P from the oceans (Filippelli and Delaney, 1996; Faul et al., 2003). The conversion of more labile forms of P (organic and oxide-associated) to authigenic P is time dependent (Filippelli and Delaney, 1996; Faul et al., 2003), therefore, the conversion is likely ongoing in young sediments. Because of this reorganization of P within sediments, to evaluate organic P burial and the relationships with export production and nutrient utilization, total reactive P concentrations (the sum of the P that is adsorbed or associated with oxides, authigenic P, and the remaining organic P in a sample) and accumulation rates need to be determined (Anderson et al., 2001).

Phosphorus burial and accumulation rates have been determined in a number of oceanographic settings, including continental margins (Ruttenberg and Berner, 1993; Slomp et al., 1998; Slomp et al., 2002; van der Zee et al., 2002), the open ocean (Filippelli and Delaney, 1996; Latimer and Filippelli, 2001; Tamburini et al., 2002; Faul et al., 2003), and restricted basins or anoxic settings (Filippelli, 2001; Benitez-Nelson et al., 2004) as well as for many different time intervals during the Cenozoic and Cretaceous. What has not been evaluated with rigor in the past is P geochemistry in opal-rich sediments.

Several studies have recently highlighted diatom intrinsic organic matter and nitrogen (Sigman et al., 1999; Crosta and Shemesh, 2002; Crosta et al., 2002; Robinson et al., 2004), and it is likely that there is also associated diatom intrinsic P. Organic macromolecules characterized as polyamines and called silaffins, which are P-rich, are important in silica biomineralization (Kroger et al., 2002). Silaffins recovered from cultured diatoms were only extracted when the diatom shells were dissolved (Kroger et al., 2002; Sumper and Kroger, 2004), thus potentially containing a pool of P within marine sediments that is not easily liberated by the traditional sequential extraction protocol (Ruttenberg, 1992; Anderson and Delaney, 2000). A few studies have modified the SEDEX protocol such that any opal-associated P is included in the determination of total reactive P by using a total sediment digestion of the residue to determine organic P (Schenau and De Lange, 2000; Schenau et al., 2000; Schenau and De Lange, 2001; Slomp et al., 2002; van der Zee et al., 2002). Additionally, total sediment digestions and subsequent determinations of P/Al or P/Ti ratios include opal-associated P but are not suited for understanding P diagenesis and P mobility in sediments because they are focused on total reactive P concentrations. Because diatoms dominate many moderate to high productivity settings, any opal-associated P would contribute to the total reactive P component and be related to nutrient utilization in the surface ocean. This paper is a first attempt to describe and quantify the role of opal-associated P in diatom-rich marine sediment and to explore the implications for the marine P cycle.

2. Study sites

We focused on a series of deep sea sediment cores (Fig. 1, Table 1) that span a range of latitudes, oceanographic settings, and sediment types. Ocean Drilling Program (ODP) Leg 177 sites 1089 (Subantarctic), 1093 (Polar Frontal Zone), and 1094 (Antarctic) are located in the southeastern Atlantic Ocean spanning sites well north, near, and south of the Antarctic Polar Front (APF). Sites 1093 and 1094 were likely covered at least intermittently by sea ice during glacial conditions based on reconstructions of late Quaternary sea ice extent (Gersonde and Zielinski, 2000; Gersonde et al., 2003). These sites also represent two distinct sediment types; high carbonate content with a mix of terrigenous mud and opal (1089) compared to predominantly opal-rich sediments (1093 and 1094) (Gersonde et al., 1999). As a contrast, ODP Leg 189, Sites 1170 and 1171 (Subantarctic) are located to the south of Tasmania, where the sediments are extremely carbonate-rich, averaging 93 wt% carbonate and minimal opal through the Pleistocene (Exon et al., 2001). The sites in the southeastern Atlantic Ocean all have high average sedimentation rates, ranging from 12 to 25 cm/kyr (Gersonde et al., 1999), while Site 1170 and 1171 have average sedimentation rates of 1–3 cm/kyr (Exon et al., 2001). The sites also span a range of waters depths. Site 1089 is the deepest at 4620 m and Site 1171 is the shallowest at 2150 m. All of the sediments analyzed in this study are Pleistocene in age, except ODP Leg 178, Site 1095 which represents Miocene–Pliocene (8–3 Ma) age sediments. Site 1095 was recovered from a sediment drift on the northwestern Pacific margin of the Antarctic Peninsula. Site 1095 sediments were characterized as a mix of sand, silt, and clay deposited by muddy turbidity currents interbedded with more massive diatom bearing silty clay interpreted as hemipelagic sediments (Barker et al., 1999). Sediments alternate between diatomaceous and terrigenous facies, and are carbonate poor (<1–2 wt% $CaCO_3$) (Barker et al., 1999). Age models are based either on oxygen isotope stratigraphy of Hodell et al. (2001), available biostratigraphic data (Flores and Marino, 2002; Zielinski and Gersonde, 2002), or magnetostratigraphy (Acton et al., 2002).

3. Methods

Sequential extractions for P geochemistry were performed on samples from all sites using the procedure
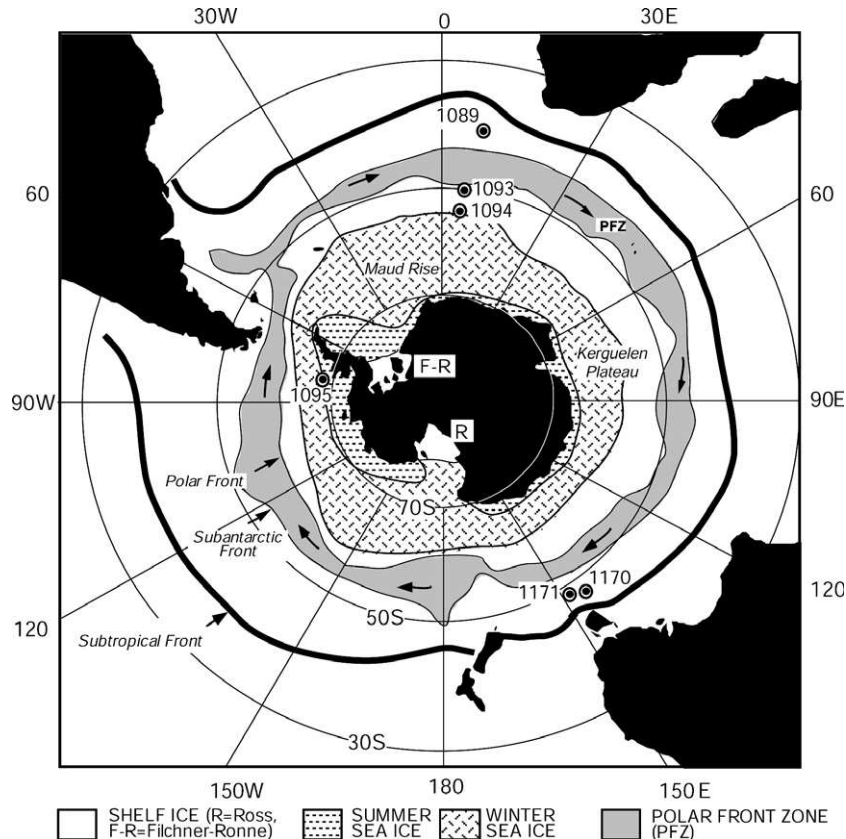
Fig. 1. Ocean drilling program (ODP) study site locations in the Southern Ocean (modified from Gersonde et al., 1999).

Table 1
Study site locations and water depth

ODP site	Location	Water depth (m)	Primary lithology	Average sedimentation rates (cm kyr^{-1})
1089	41°S, 9°E	4620	Mixed carbonate	13
1093	50°S, 5°E	3626	Opal	25
1094	53°S, 5°E	2807	Opal	14
1095	66°S, 78°W	3840	Alternating terrigenous and diatomaceous facies	5
1170	48°S, 146°E	2704	Carbonate	3
1171	47°S, 147°E	2150	Carbonate	1

outlined by Anderson and Delaney (2000) after Ruttenberg (1992) to separate and analyze 4 different sedimentary components of P (Table 2). Dried and crushed sample was weighed into new 15 mL polyethylene centrifuge tubes. Samples with reagents were shaken on an orbital shaker for the prescribed amount of time and then centrifuged. All supernatants were decanted into acid cleaned polyethylene bottles, pooled, and saved for analysis. A Shimadzu scanning UV-Visible Spectrophotometer was used for the determination of P concentrations for authigenic P, organic P, and detrital P (steps II–IV) from the sequential P extraction using the molybdate blue technique for color development (Strickland and Parsons, 1972). Dithionite-

extractable P (step I) concentrations were determined by ICP-AES because the citrate dithionite solution interferes with color development.

Extractions to determine P within opal (opal-associated P) were performed on a subset of samples from sites except 1170 using sample residues from the standard P extraction. Sample residues were rinsed with Milli-Q water, centrifuged, and decanted twice before 10 mL of 1.5 M NaOH was added (Tables 2 and 3). The samples were loosely capped and heated for 2 h in a water bath at 85 °C. Samples were capped and shaken every 30 min. The samples were centrifuged and analyzed using the molybdate blue technique (as described above) the same day to avoid problems with opal re-precipitation.

Opal-associated P was also determined on sample residues following the procedure of Mortlock and Froelich (1989) using 10 mL of 2 M Na_2CO_3 for samples from sites 1093 and 1094. Sample concentrations of P were determined using an ICP-AES. The same residues were then reacted using the NaOH method above and resulted in more P being liberated. The subsequent NaOH method liberated additional P. For the samples that were analyzed by both methods, the reported opal-associated P concentrations are the sum of the two steps. It should be noted that NaOH is capable of leaching P from any lithogenic material that is present; however, samples have already been treated with HCl to quantify the detrital P component.

Table 2
Extraction steps (after Mortlock and Froelich, 1989; Ruttenberg, 1992; Anderson and Delaney, 2000)

Step	Reagents	P component isoloated
Oxide-associated	10 mL CDB solution (6 h) (0.22 M Na citrate, 1 M $NaHCO_3$, 0.13 M Na-dithionite), 10 mL of 1 M $MgCl_2$ (2 h), 10 mL H_2O (2 h)	Adsorbed and reducible or reactive Fe-bound P
Authigenic	10 mL of 1 M Na-acetate buffered to pH 4 w/acetic acid, 10 mL of 1 M $MgCl_2$ (2 h)-twice, 10 mL H_2O (2 h)	Carbonate fluorapatite (CFA), biogenic hydroxy apatite, and $CaCO_3$-bound P
Detrital	10 mL of 1 M HCl (16 h)	Detrital P
Organic	1 mL 50% (w/v) $Mg(NO_3)_2$, dry in low oven, ash at 550 °C (2 h), add 10 mL of 1 M HCl	Organic P
Opal-associated	10 mL of 1.5 M NaOH or at 85 °C (2 h), or 10 mL of 2 M Na_2CO_3 at 85 °C (5 h) followed by 10 mL of 1.5 M NaOH, at 85 °C (2 h)	Opal-associated P
Residual	5 mL HNO_3, 4 mL HF, 1 mL HCl	P remaining following extraction steps

Table 3
Methods used to determine opal-associated P

1.5 M NaOH	1089, 1171, subset of 1093 and 1094
2 M Na_2CO_3 + 1.5 M NaOH	Subset of 1093 and 1094
Total digestion of residue following SEDEX	Subset of 1093 and 1170

Any P that was not completely leached by the HCl step would be included in the opal dissolution step.

Another subset of extraction residues were transferred to microwave digestion vessels using Milli-Q water from Site 1093 and 1170. Using an MDS 2000 Microwave Digestion System and concentrated trace-metal grade HNO_3, HF, and HCl following EPA SW846 Method 3052 the residues were dissolved and P concentrations were determined using ICP-AES. All P concentrations from Site 1170 ($n = 14$) were below the analytical detection limit (0.09 μmol P g^{-1}), which was calculated as three times the standard deviation of the blank value. P concentrations for Site 1093 are assumed to be opal-associated P because concentrations are similar to the concentration by other methods listed above.

Accuracy was evaluated based on comparison to the long-term results from a consistency standard included in all P extractions performed. Relative error for the long-term means were ±4% for oxide associated P, ±10% for authigenic P, ±11% for detrital P, and ±6% for organic P. Although based on limited standard data, the relative error for the opal dissolution step was ±13%. In addition, the range of concentrations for the opal-associated P (Table 4) fall within the ranges reported by Kryc et al. (2003) for the equatorial Pacific (carbonate-rich setting) and Palmer Deep near the Antarctic margin (mixed terrigenous and opal setting).

Total reactive P accumulation rates for Site 1089 for the last 80 kyr were determined following the approach of Sachs and Anderson (2003) using [230]Th data from TN057-21 to calculate [230]Th normalized fluxes at Site 1089 by correlating the carbonate records from the two sites (Hodell et al., 2001). TN057-21 is also located in the Cape Basin, 76 km WSW of Site 1089 (Sachs and Anderson, 2003). Sachs and Anderson (2003) used a two tie point alignment procedure to synchronize the carbonate records in the depth domain. Sediment focusing is especially problematic in the Southern Ocean and has been described by several authors (e.g., Francois et al., 1993; Kumar et al., 1995; Frank et al., 1999; Chase et al., 2001). Instead of using age model based sedimentation rates to calculate accumulation rates, it is more appropriate to use [230]Th-normalized fluxes because they correct for sediment redistribution and provide a more accurate estimate of particle flux (Francois et al., 2004).

4. Results and discussion

Using the modified SEDEX protocol of Anderson and Delaney (2000), either oxide-associated or authigenic P dominates extractable P at all sites investigated (Table 5). In all cases total reactive P accounts for 89% or more of total extractable P. However, following the opal dissolution step, total reactive P concentrations always increased (when the sediments contained opal) regardless of the method used. Furthermore, the dominant sedimentary P component (average >50%) in Pleistocene age opal-rich sediments (1093 and 1094) is opal-associated P (Table 6), while the Site 1095 Miocene–Pliocene age sediments averaged only 19% opal-associated P. Even though Site 1095 has average opal-associated P concentrations similar to

Table 4
Average P concentrations and standard deviations (μmol P g^{-1})

ODP site	# samples analyzed	Oxide P	Oxide P SD	Authigenic P	Authigenic P SD	Organic P	Organic P SD	Detrital P	Detrial P SD	Opal P	Opal P SD
1089	55	8.88	0.76	8.05	0.13	1.94	0.02	0.75	0.02	2.30	0.03
1093	98	1.06	0.25	1.65	0.04	0.33	0.01	0.28	0.01	4.00	0.02
1094	49	2	0.2	2.04	0.05	0.67	0.01	0.61	0.01	5.37	0.03
1095	28	9.03	0.78	14.84	0.11	1.24	0.08	2.88	0.02	6.11	0.02
1171	16	3.09	0.13	4.11	0.04	0.23	0.02	0.20	0.01	0.16	0.02

Table 5
Average P content using SEDEX (Ruttenberg, 1992; Anderson and Delaney, 2000)

ODP site	# samples analyzed	Oxide (%)	Authigenic (%)	Organic (%)	Detrital (%)	Total reactive P[a] (%)
1089	89	45	42	10	4	97
1093	156	31	47	10	12	88
1094	77	38	38	11	14	86
1095	58	30	55	11	5	96
1171	55	41	53	3	3	98

[a] Total reactive P is the sum of the oxide associated, authigenic, and organic P fractions.

Table 6
Adjusted P content

ODP site	# samples analyzed	Oxide (%)	Authigenic (%)	Organic (%)	Detrital (%)	Opal-associated (%)	Opal content (wt%)
1089	55	45	34	3	8	10	3–23
1093 (digestion for residual P and opal extraction)	98	11	21	4	5	60	41–87
1094	49	17	20	6	6	52	22–96
1095	28	28	43	9	4	19	18–60
1171	16	37	56	2	3	2	Minor

Site 1093 and 1094 (Fig. 2), the relative contribution of opal-associated P is typically lower (Table 6). One explanation is that the Site 1095 samples are diagenetically more mature. Over time, P is redistributed into different sedimentary pools. In carbonate-rich sediments, this sink-switching usually explains the downcore gain in authigenic and/or oxide associated P at the expense of organic P (Filippelli, 2001). An unknown is the influence of opal dissolution and diagenesis (i.e. the conversion of amorphous opal (opal A) to opal CT as well as the formation of authigenic silicates) on P retention and redistribution in sediments. For example, silica diagenesis occurs most rapidly in settings with high geothermal gradients while P redistribution in sediments is time dependent; however, early diagenetic cherts and porcellanites have been observed in the South-

ern Ocean (Bohrman et al., 1994). There are porcellanite (opal-CT) concretions found in sediments recovered from Site 1094, which may provide an opportunity to study the effects of opal diagenesis on P redistribution, however, the discreet porcellanite layers were not sampled for this study. Because Site 1095 samples are older, they have had more time to undergo opal dissolution, silica diagenesis, and potentially P redistribution.

The carbonate rich samples have much lower relative contributions of opal-associated P. Site 1089, with minor to moderate opal, averaged 10% opal-associated P, while Site 1171 has minimal opal content and correspondingly low opal-associated P concentrations averaging ∼2% of total extractable P. There is limited data available for Site 1171 because there was minimal sample residue remaining
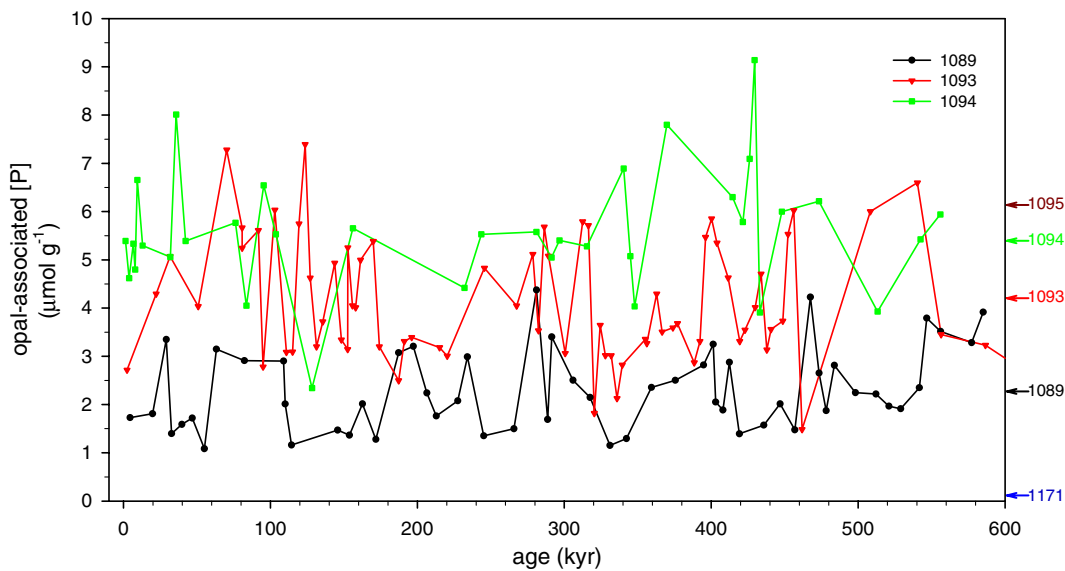

Fig. 2. Opal-associated P concentrations (μmol P g^{-1}) plotted for sites 1089, 1093, and 1094 versus age. The arrows at right represent the average value for all samples analyzed except those for Site 1170 because all of the concentrations were below the analytical detection limit. Ages for Sites 1089, 1093, and 1094 are based on the age models of Hodell et al. (2001), Flores and Marino (2002), or Zielinski and Gersonde (2002). Average standard deviations for Sites 1089 and 1094 were 0.03 μmol P g^{-1}, and average standard deviations for Sites 1093, 1095, and 1171 were 0.02 μmol P g^{-1}.

following the standard extraction steps. For the 16 samples (out of a total of 55 samples) from Site 1171 that have opal-associated P data, the average P concentration of opal-associated P is 0.16 μmol P g^{-1}, which is more than an order of magnitude lower than all of the concentrations observed at the other sites (Fig. 2) and near the analytical detection limit of 0.09 μmol P g^{-1}. The relationship between low opal and low opal-associated P found in Site 1171 indicates that the additional P extracted and attributed to opal-P at the other study sites is not likely a procedural or reagent blank artifact but rather is opal-associated P.

Comparison between opal-associated P and opal content (Fig. 3) do not reveal a clear relationship; however, sites with higher average opal content have higher opal-associated P concentrations (Tables 1 and 5). In fact, cross plots of the opal-associated P and opal content at Site 1095 reveal no relationship at all (Fig. 4). One explanation for this lack of correspondence is that opal dissolution readily occurs within sediments, therefore, opal-associated P may have been released to pore waters following dissolution where it then became associated with oxides or oxyhydroxides or converted to CFA. The degree of opal dissolution can be highly variable within a site and between sites because of varying environmental factors that include pressure and temperature, but also diatom surface area and the incorporation of Al in frustules including secondary uptake of Al during early diagenesis (Dixit et al., 2001; Dixit and van Cappellen, 2002).

Following the opal dissolution step, total reactive P concentrations increased at Sites 1089, 1093, 1094, and 1095 (Fig. 5, Table 7). The general down core trends do not change significantly, however, total reactive P concentrations at sites 1093 and 1094 increase on average by 100–200%. Total reactive P concentrations at Site 1089 increase by ~10%, while concentrations increase by ~25% at Site 1095. By not including opal-associated P in the calculation of total reactive P, P burial at these four sites was severely underestimated for most samples.

A danger inherent to using sequential extractions is that the steps are operationally defined by what is in solution following extractions by reagents of a particular strength and in a particular reaction order (Martin et al., 1987). Until the residual P is better understood, all of the potential sources for this P need to be explored, including diatom intrinsic P, organic P that was not fully extracted, and mineral P. Silaffin molecules within biogenic opal are a potential source for diatom intrinsic P (Kroger et al., 2002). However, it is presently unknown how much silaffins can contribute to the observed opal-associated P. It is also possible that the residual P is organic P that is unrelated to silaffins and that was not liberated during the organic P extraction step be-

cause it was protected and contained within diatom frustules and could only be extracted following opal dissolution. Another potential source of the residual P is mineral P that was not fully extracted by the HCl used for the detrital P extraction step. If the residual P in these Southern Ocean samples is resistant P-bearing minerals, then the assumption that most P reaching the seafloor is associated with organic material needs to be revisited. As much as 80% of the extractable P at Site 1093 (Fig. 3b), for example, is residual P assumed to be associated with opal. Additionally, results from Site 1094 indicate that it is unreasonable to invoke resistant mineral-P as the driver of the opal-P results. Some intervals at this site reach 98% opal (Fig. 3c), and thus the maximum non-opal fraction of this sediment is 2%. For the sake of calculation, we will assume that the entire non-opal fraction is resistant terrigenous material. Given the concentration of opal-P of about 8 μmol P g^{-1} in this interval and a total non-opal mass of 0.02 g g^{-1} for this sample (0.98 g opal), we calculate a non-opal P concentration of 12,400 μg P g^{-1} sediment, which converts to a concentration of 1.24 wt% P in this interval. This calculated value would be 7–16 times greater than the average crustal value for P of 0.08–0.18 wt% P (Wedopohl, 1995; Faure, 1998); this value is unreasonable given any end-member resistant mineral type, and would compound the calculated opal-P values to extremely high values in intervals where the opal content is relatively low.

Because biogenic opal and biogenic carbonate undergo different diagenetic pathways, it is conceivable that sedimentary retention and redistribution of P within these sediments would also be influenced by sediment type. In carbonate-rich sediments, the carbonate acts as a template for CFA formation. In opal-rich sediments, this template would be absent possibly resulting in much slower CFA formation. Also, if opal frustules themselves protect opal intrinsic P, P release to pore waters would occur more slowly and be limited by the extent of opal dissolution and diagenesis. Also, as mentioned previously, the effects on P sedimentary distribution of the conversion from opal A to opal CT within sediments is unknown. However, it seems likely that P diagenesis in opal-rich settings may occur more slowly than in carbonate dominated settings because opal-P may follow a different diagenetic pathway.

5. Phosphorus accumulation rates and opal-associated P

The average total reactive P accumulation rate during the last glacial interval was 11.9 μmol P cm^{-1} kyr^{-1} without opal associated P and 13.4 μmol P cm^{-1} kyr^{-1} includ-

Fig. 3. Downcore opal-associated P (black circles), % of total extractable P that is opal-associated (blue triangles), and opal content (red squares) versus depth for (a) 1089, (b) 1093, (c) 1094, and (d) 1095. Opal content for sites 1089, 1093, and 1094 were determined by XRD peak intensity (Gersonde et al., 1999). Site 1095 sediments alternate between terrigenous and diatomaceous. The terrigenous content was determined by Hassold et al. (2004) and opal content was calculated by difference. Opal content has been smoothed using a 3-point moving average for Site 1095. Data for Site 1170 and 1171 are not shown because there is limited data available and because both sites have low opal content and low opal-associated P concentrations that are either at or below the analytical detection limit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

ing opal associated P. Assuming the Southern Ocean, defined as the ocean area south of the subtropical convergence zone, comprises 22% of the global ocean and

extrapolating Site 1089 glacial P accumulation rates to the entire Southern Ocean, glacial burial rates for the Southern Ocean were 0.95×10^{10} mol P yr^{-1} without opal
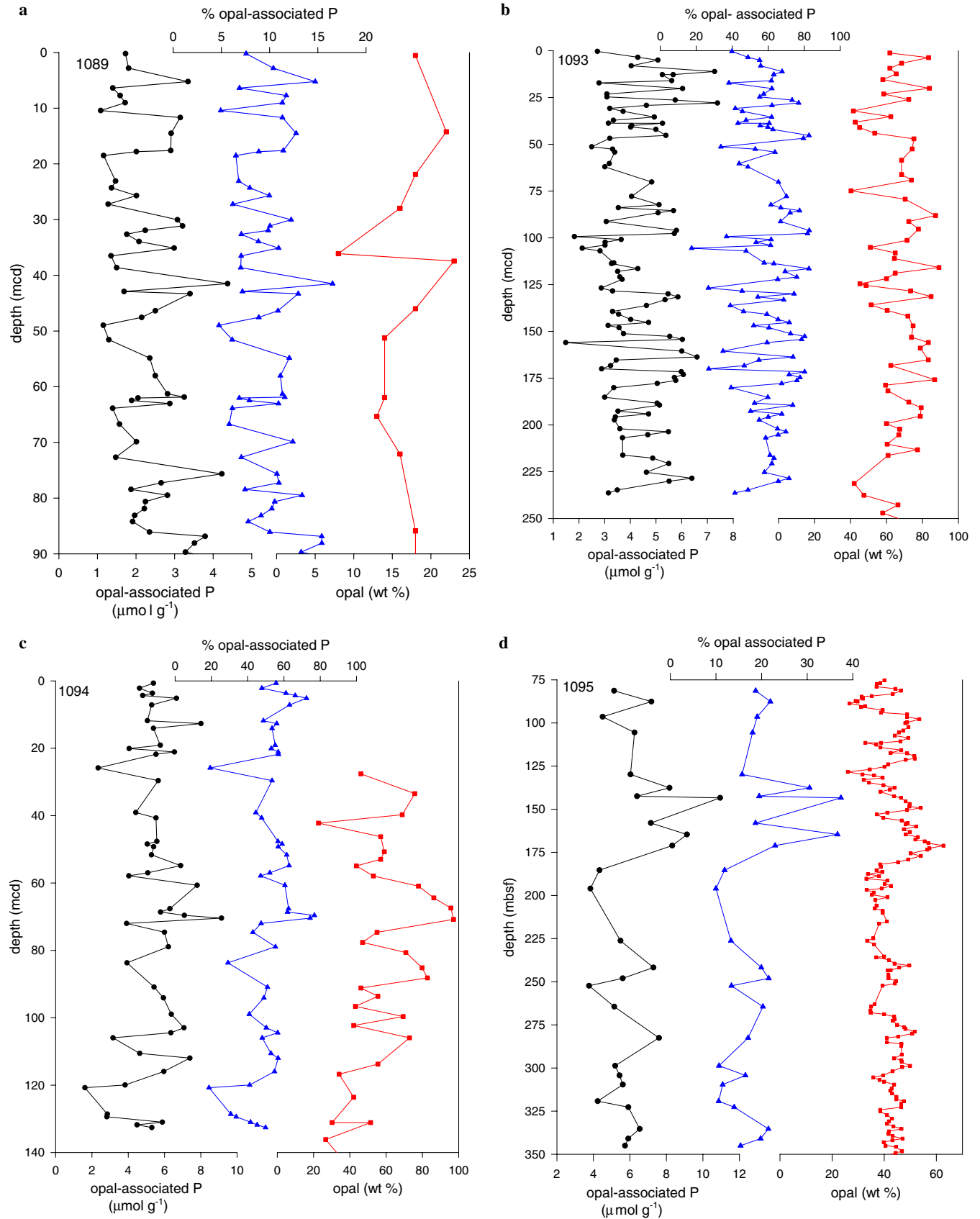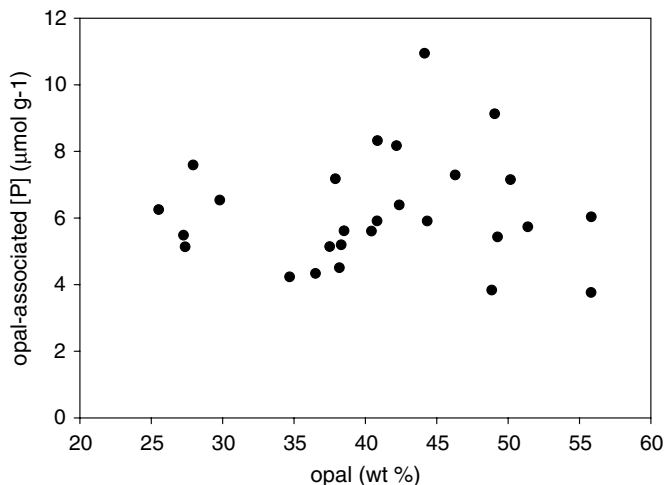
Fig. 4. Opal associated P and opal content at Site 1095. Despite the fact that average opal-associated content increases as average opal content increases (Fig. 2), there is no apparent relationship between opal-associated P and opal content of the individual values at a given site.

associated P and 1.06×10^{10} mol P yr^{-1} including opal associated P. The P burial fluxes without inclusion of opal associated P are underestimated by $\sim 10\%$ for the last glacial interval and would be underestimated even more at

more southerly sites containing greater amounts of opal associated P. Filippelli and Delaney (1996) determined P burial rates in the equatorial Pacific of 0.6×10^{10} mol P yr^{-1}. Equatorial Pacific samples commonly have biogenic opal content >10 wt% (Schroeder et al., 1997), if some of the biogenic opal is from diatoms (rather than radiolarians, which are not the predominant biogenic opal component in the Southern Ocean cores studied here), P burial in the equatorial Pacific and other high productivity settings may have been underestimated by 10% or more because opal-associated P was not routinely determined. Even after adjusting the equatorial Pacific P fluxes by 10–25%, the Southern Ocean P burial rates would still be significantly higher than those observed in the equatorial Pacific Ocean (0.66–0.8×10^{10} mol P yr^{-1} in the equatorial Pacific compared to 1.06×10^{10} mol P yr^{-1} in the Southern Ocean), suggesting that the Southern Ocean sediments are a more important sedimentary P sink on glacial/interglacial time scales than previously considered because of the presence of opal-associated P. The Southern Ocean accounts for most of the biogenic opal burial in the deep-sea (>70%) (DeMaster, 2002); therefore, it is expected that the impact of opal-associated P would be most significant in the Southern Ocean. However, it is important to point out that temporal variability in opal burial has not been
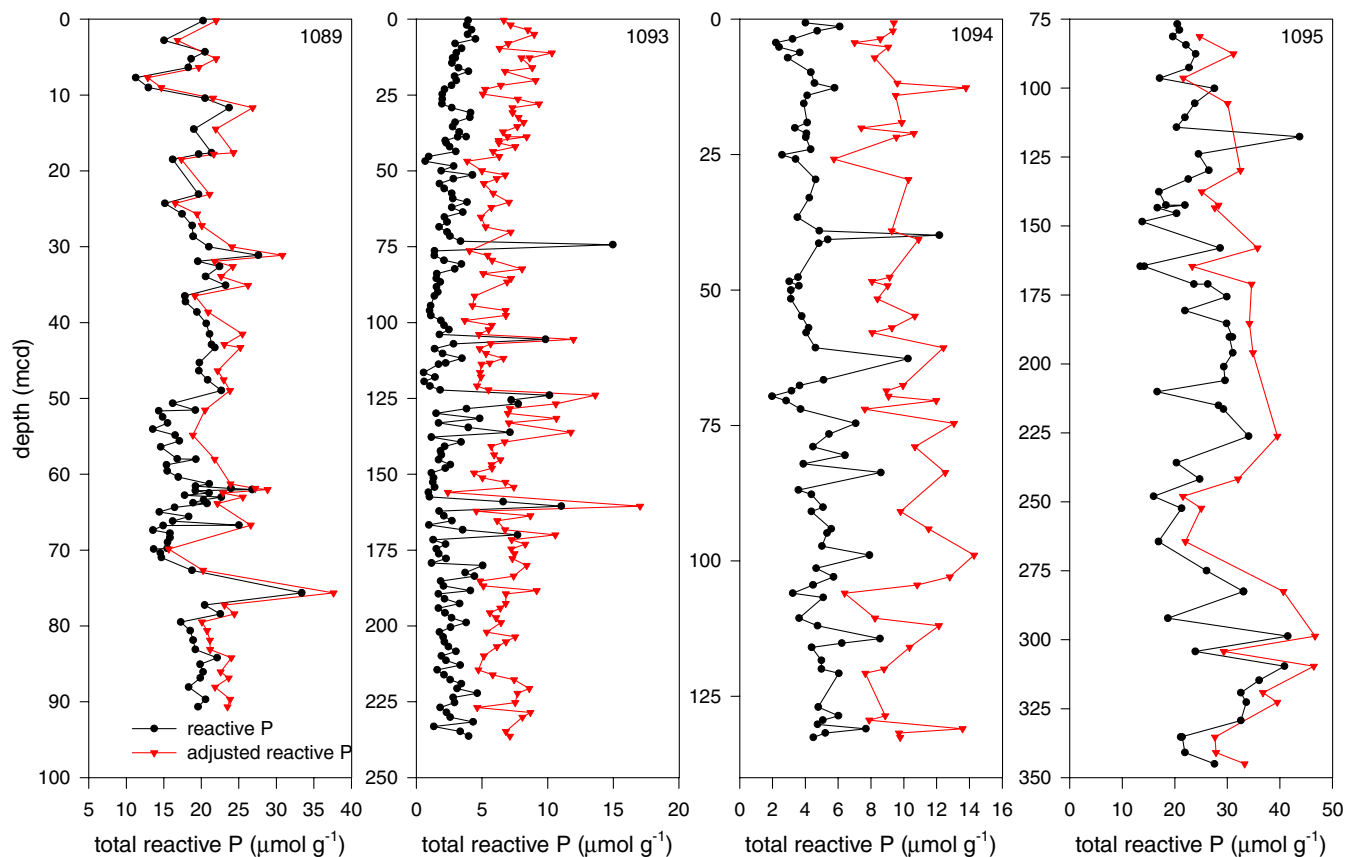

Fig. 5. Total reactive P concentrations with (red triangles) and without (black circles) opal-associated P versus depth. Data for Site 1170 and 1171 are not shown because there is limited data available and because both sites have low opal content and low opal-associated P concentrations that are either at or below the analytical detection limit. Depths for Site 1095 are in mbsf. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

Table 7
Average reactive and adjusted reactive P

ODP site	Total reactive P[a] ($\diamondsuit$ mol g^{-1})	Adjusted total reactive P[b] ($\diamondsuit$ mol g^{-1})	Average total reactive P increase (%)	Minimum increase (%)	Maximum increase (%)
1089	20.1	22.4	11	5	21
1093	2.8	7.0	206	22	767
1094	4.4	9.8	135	27	359
1095	25.2	31.3	27	12	66

[a] Total reactive P is the sum of oxide-associated, authigenic, and organic P.
[b] Adjusted total reactive P is the sum of total reactive P and opal-associated P.

equivocally determined for the late Quaternary, with estimates ranging from higher opal burial during glacial intervals (Charles et al., 1991; Kumar et al., 1995) to lower opal burial during glacial intervals (Mortlock et al., 1991; Bareille et al., 1998; Chase et al., 2003).

P fluxes were also determined for Site 1095 (Fig. 6). The samples investigated here fall within the late Miocene–early Pliocene biogenic bloom (8–3 Ma). Similar to other P accumulation records (Filippelli and Delaney, 1994), the time interval from 8–6 Ma appears to be a time of elevated P burial compared to late Quaternary P burial rates (Site 1089, see above). Maximum P accumulation rates fall within the range of values observed in the equatorial Pacific (Filippelli and Delaney, 1994) and the Indian and Atlantic Oceans (Hermoyian and Owen, 2001) for this time and within the range found in open ocean regions (see Filippelli, 1997 and references therein). Total reactive P fluxes and burial rates with and without adjustment for opal-associated P differ by 20–30% on average. While it is not possible to evaluate how much P burial increased during the biogenic bloom event, because samples prior to and following the event were not analyzed, it is clear that Southern Ocean P burial was significant during the Neogene and further substantiates the observation that opal-associated P is

an important sedimentary P pool that also needs to be quantified over longer time scales.

6. Implications

The presence of a diatom intrinsic opal phase that is not completely extracted by traditional extraction schemes has significant implications for our understanding of the P mass balance for the oceans and the residence time of P in the oceans. Diatoms are important primary producers in many high productivity ocean environments, either because they are the dominate phytoplankton or because they are episodically abundant. If there is an opal-associated P reservoir that has not been quantified, then P burial in high productivity sediments may have been underestimated by sequential extractions. In settings that are dominated by calcareous phytoplankton, but with some diatoms, similar to Site 1089, P burial might be underestimated by as much as 5–20% (Fig. 3a, Table 7). However, in settings dominated by diatoms, Sites 1093 and 1094 (Fig. 3b and c), P burial might be underestimated by a factor of 2–3 or more (Table 7). Even in older sediments (Site 1095) that have presumably undergone significant diagenetic alteration, P burial could be underestimated by ~25% if opal-associat-
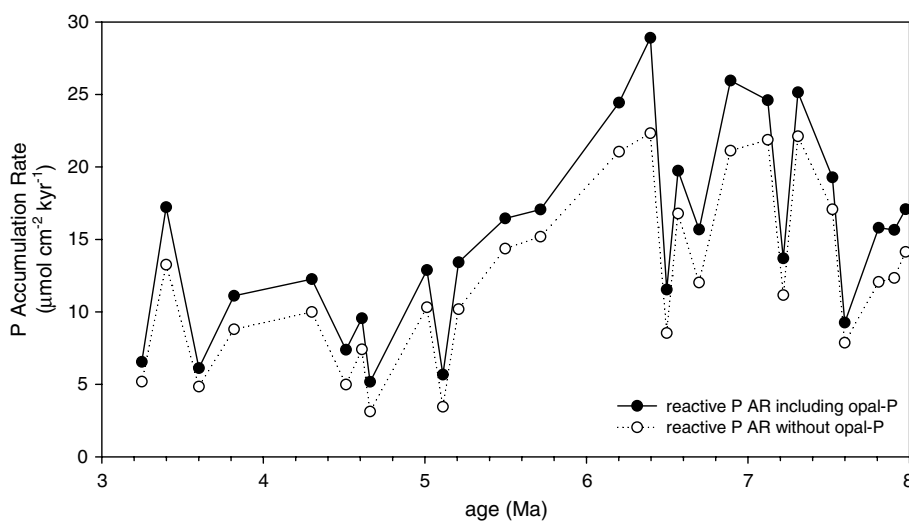

Fig. 6. P accumulation rates at Site 1095 for 8–3 Ma. Filled circles and the solid line represent total reactive P accumulation rates adjusted for the presence of opal-associated P while open circles and the dashed line are the uncorrected total reactive P accumulation rates.

ed P is not determined. Using the SEDEX reaction scheme, therefore, potentially underestimates P burial, on average, by a minimal 5% to as much as 767% depending on opal content and age of the sediments. By including opal-associated P as a contributor to total reactive P, P burial in the world's oceans should be higher especially considering the prevalence of diatoms in high productivity settings. Furthermore, by quantifying opal-associated P burial, the residence time of P in the oceans may be shorter than previously suspected because this pool has not been identified as a significant removal mechanism for P from the oceans. Alternatively, if future research shows that the residual P is related to resistant P-bearing minerals or an authigenic silicate rather than biogenic opal, detrital P fluxes and P diagenesis in opal-rich sediments will need to be further evaluated.

7. Conclusions

Analysis of residual sediment remaining after completion of a sequential extraction protocol for P resulted in additional P being liberated from the sediments that underwent an opal dissolution step. This additional P is assumed to be associated with biogenic opal, although other sources may contribute to the residual P including organic P or mineral P not fully extracted by previous steps. If the residual P is found to be mineral P and not opal-associated or organic P, then the detrital flux of P to the oceans needs to be revisited, however, it was demonstrated that it is unreasonable for all of the residual P found in opal-rich sediments to be in a mineral form. Alternatively, assuming the residual P is opal associated P or organic P, then total reactive P burial has likely been underestimated by traditional extraction protocols, especially in high productivity diatom-rich settings. For example, in Pleistocene age, opal-rich sediments from the Southern Ocean P burial is underestimated, on average, by 200% while in Miocene–Pliocene age sediments P burial is underestimated by only 25% on average. This underestimation of total reactive P burial in opal-rich sediments may mean that current estimates of the residence time for P in the oceans are too long. Additionally, the P mass balance for the oceans needs to be re-evaluated to include P burial in opal-rich sediments.

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