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Phosphorus burial as a function of paleoproductivity and redox conditions in Arabian Sea sediments

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Abstract—In this study the response of sedimentary phosphorus (P) burial to changes in primary productivity and bottom water oxygen concentrations during the Late Quaternary is investigated, using two sediment cores from the Arabian Sea, one recovered from the continental slope and the other from the deep basin. The average solid-phase P speciation in both cores is similar, authigenic and biogenic (fish debris) apatite make up the bulk of the P inventory (ca. 70%);whereas P adsorbed to iron oxides, organic P, and detrital apatite constitute minor fractions. Postdepositional redistribution has not significantly altered the downcore distribution of total solid-phase P. Phosphorus burial efficiencies are generally lower during periods of increased paleoproductivity. This is caused by (a) partial decoupling of the P export flux, consisting primarily of particulate organic P, and the P burial flux, consisting primarily of biogenic and authigenic apatite; and (b) the lack of increased rates of authigenic CFA formation during periods of higher P deposition. In addition, fluctuations in bottom water oxygen concentrations may have affected P burial in continental slope sediments. The results of this study indicate that higher primary productivity induces more efficient P cycling. On time scales exceeding the oceanic P residence time, this process may induce higher surface water productivity, thus creating a positive feedback loop. In the Arabian Sea, this feedback mechanism may have contributed to changes in sea surface productivity on sub-Milankovitch time scales because P, regenerated on the continental slopes of the Oman and Somalian coastal upwelling zones, is reintroduced into the photic zone relatively fast. *Copyright © 2005 Elsevier Ltd*

1. INTRODUCTION

Primary productivity in the oceans is governed by the availability of nutrients in the photic zone. Nitrogen is the limiting nutrient in most present-day coastal waters (Howarth, 1988). In contrast though to nitrogen, phosphorus forms no important gaseous phases in the natural environment, and the oceanic P mass balance is, therefore, solely governed by the input from fluvial and eolian sources and burial in sediments (e.g., Froelich et al., 1982; Delaney, 1998). Phosphorus availability is generally considered to be the main factor controlling net primary productivity in the oceans on geological time scales because long-term shortages of nitrogen are replenished by nitrogen fixation from the atmosphere (Holland, 1978; Howarth et al., 1995; Tyrrell, 1999). Marine productivity, in turn, determines the burial of organic carbon and controls the atmospheric CO_2 and O_2 content. Detailed knowledge of phosphorus cycling in the oceans thus provides a better understanding of the biogeochemistry of the ocean and atmosphere, on geological time scales (e.g., Van Cappellen and Ingall, 1994; Van Cappellen and Ingall, 1996; Colman and Holland, 2000; Ganeshram et al., 2002).

Net phosphorus removal from the oceans is governed by incorporation in particles and subsequent vertical transport, and the degree of particulate P regeneration in the water column and sediment (e.g., Froelich et al., 1982; Krajewski et al., 1994; Follmi, 1996). Sedimentary-P remobilisation processes include organic matter decomposition, phosphate desorption from iron

oxides, and dissolution of fish debris (e.g., Froelich et al., 1988; Van Cappellen and Berner, 1988). Phosphorus burial is dependent on several environmental factors, such as sedimentation rate, sediment porosity, microbial activity, the occurrence of authigenic apatite formation, bioturbation rates, and bottom water oxygen conditions (e.g., Filippelli and Delaney, 1994; Krajewski et al., 1994). The influence of the oxidation state of marine sediments on P burial is a much debated topic. Benthic regeneration of phosphorus is more extensive when bottom waters are oxygen-depleted, resulting in a lower P burial efficiency (Ingall and Jahnke, 1994; Colman and Holland, 2000). Enhanced loss of P from sediments over long periods of bottom water anoxia (i.e., exceeding the oceanic P residence time) will lead to an increased supply of phosphate to the surface waters, which may promote higher biologic productivity (Ingall et al., 1993; Ingall and Jahnke, 1997). This positive feedback between water column anoxia, benthic P regeneration, and marine productivity may link organic-rich sediments to anoxic bottom water conditions (Ingall and Jahnke, 1994; Ingall and Jahnke, 1997; Slomp et al., 2002).

In this study, phosphorus burial was investigated in the northern Arabian Sea using two sediment cores taken from the Pakistan continental slope and the deep Arabian Basin, both covering the last 120 kyr. The Arabian Sea is one of the most productive ocean basins of the world. During Northern Hemisphere summer, strong south westerly monsoon winds cause intense upwelling offshore Somalia and Oman (e.g., Wyrtki, 1973; Slater and Kroopnick, 1984). This causes high-seasonal productivity throughout the Arabian Sea (e.g., Qasim, 1982). High downward fluxes of organic matter, in combination with a sluggish intermediate water ventilation, result in an intense

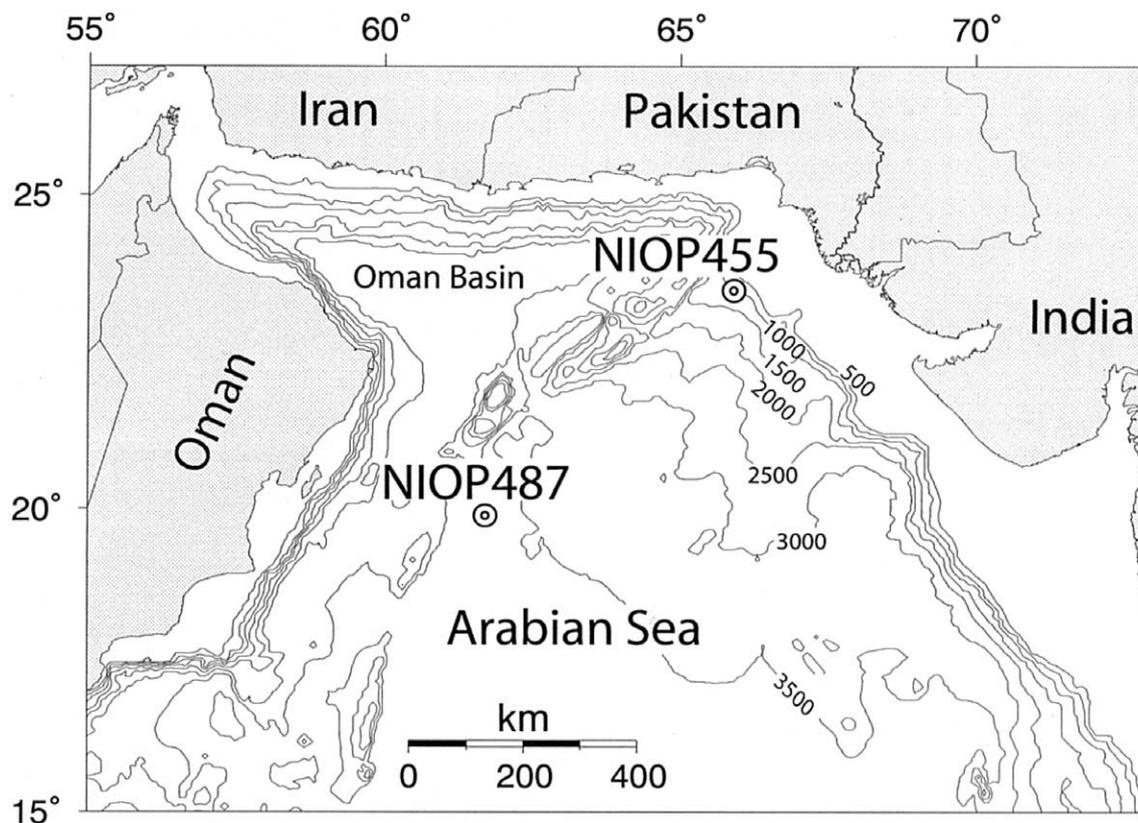* Author to whom correspondence should be addressed (reichart@geo.uu.nl).

Fig. 1. Sample locations of NIOP 455 (Pakistan continental margin) and NIOP 487 (Arabian Basin). Depth contours are drawn with 500 m intervals.

Oxygen Minimum Zone (OMZ) between 150 and 1250 m water depth (e.g., Slater and Kroopnick, 1984), with bottom water oxygen (BWO) concentrations <2 μM (e.g.Van Bennekom and Hiehle, 1994). Sediment core studies have revealed large fluctuations in paleoproductivity during the Late Quaternary (e.g., Shimmield, 1992; Emeis et al., 1995; Reichart et al., 1998). Frequency analysis has shown that paleoproductivity records from the Arabian Sea exhibit a strong 23-kyr signal, indicating that changes in surface water productivity primarily reflect precession controlled changes in summer monsoon upwelling (e.g., Clemens et al., 1991; Reichart et al., 1998). The intensity and vertical extension of the OMZ have strongly varied during the Late Quaternary as a result of the differences in the organic carbon rain rate and deep winter mixing (Altabet et al., 1995; den Dulk et al., 1998; Reichart et al., 1998; Reichart et al., 2002a). Accordingly, continental slope sediments have periodically experienced oxic and suboxic bottom water conditions. Sediment records from the Arabian Sea thus provide an excellent opportunity to elucidate the processes that control P removal from the oceans under different paleoenvironmental conditions.

2. MATERIAL AND METHODS

2.1. Sample Locations

The two piston cores selected for this study were taken during the Netherlands Indian Ocean Program (NIOP) in 1992. Piston core 455 (NIOP455) was taken on the continental slope of the Pakistan Margin

(23°33′3N, 65°57′2E) from a water depth of 1002 m, presently situated in a low-oxygen environment (BWO <2 μM). Piston core 487 (NIOP487) was recovered from the central Arabian Basin (19°54′.8N, 61°43′.3E) from a water depth of 3570 m, and the sample site is located well below the present-day OMZ (BWO $= 151$ μM). The locations of the sample sites are shown in Figure 1. The sediments consist mainly of homogeneous, light-greenish hemipelagic mud interbedded by darker organic-rich intervals. In NIOP455 most of these darker intervals are finely laminated.

2.2. Solid-Phase Analysis

Samples for solid-phase analyses were taken at regular intervals of 5 to 10 cm, giving a temporal sample resolution of 0.5 to 2 kyr. Porosity and dry bulk density of the sediment were calculated by measuring weight loss of fixed volume samples after freeze-drying. Dried samples were powdered in an agate mortar, and subsamples were taken for geochemical analyses after homogenization. After removal of inorganic carbon with 1 M HCl, organic carbon (C_{org}) contents were measured with a NA 1500 NCS analyser (relative errors $<1\%$). Bulk concentrations of P were determined by total digestion of 250 mg sample in 5 mL of a 6.5 : 2.5 : 1 mixture of $HClO_4$ (60%), HNO_3 (65%), and H_2O, and 5 mL HF (40%) at 90°C. After evaporation of the solutions at 190°C on a sand bath, the dry residue was dissolved in 50 mL 1 M HCl. The resulting solutions were analysed with a Perkin Elmer Optima 3000 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). All results were checked using international (SO1, SO3) and in-house standards. Relative errors for duplicate measurements are better than 3%. The chronology of the piston cores is based on $\delta^{18}O$ records (Reichart et al., 1998; Schenau et al., 2002). Mass accumulation rates (MARs) were calculated by multiplying linear sedimentation rates (LSRs) with dry bulk densities.

The solid-phase speciation of P and Fe was examined in sediment

samples from one interglacial and two glacial intervals, using a 5-step sequential extraction scheme. Samples from each core were selected that were deposited contemporaneously (with exception of two samples in the interglacial interval). About 125 mg of dried and ground sediment was subsequently extracted with (1) 25 mL 2 M NH_4Cl (pH = 7, repeated 8 times), (2) 25 mL citrate dithionite buffer (CDB, pH = 8), (3) 25 mL 1 M Na-acetate (pH = 4), 4) 25 mL 1 M HCl, and (5) 20 mL $HF/HNO_3/HClO_4$ mixture. After extraction steps 2, 3, and 4, the sediment was rinsed with 2 M NH_4Cl (pH = 7) and demineralised water to prevent readsorption of phosphate. This extraction scheme is an adaptation of the SEDEX method developed by Ruttenberg (Ruttenberg, 1992) for marine sediments. The 2M NH_4Cl extraction (step 1) was inserted to determine the P fraction associated with biogenic (fish debris) apatite (Schenau and De Lange, 2000). All extracted solutions were analysed with ICP-AES. Precision for P was generally better than 5%, except for step 2 and 3 (10%). The recovery for all extraction steps with respect to total P varied between 80 and 90%. This deficit is not caused by sample loss during the extraction procedure but is due to systematic errors in the measurements of low-P concentrations by ICP-AES. Iron oxide contents (reactive iron) were determined from the iron concentration extracted in step 2 (Na-dithionite). Organic phosphorus was determined as the difference between 1 M HCl extractable P before and after ignition of the sediment (550°C, 2h; Aspila et al., 1976). All measurements were done in duplicate (precision better than 2%). Relative errors for samples containing low-organic phosphorus concentrations are large (up to 50%) because they are calculated as the difference between two large values.

3. RESULTS AND DISCUSSION

3.1. Burial of Total Solid-Phase P

Total solid-phase P concentrations in NIOP455 vary from 700 to 2000 ppm and are generally higher in the organic-rich intervals (Fig. 2). The correlation between C_{org} and total solid-phase P (r^2 = 0.56) is significant based on the F-statistic (which determines the probability [α] that this r^2 value occurs by chance; α is infinitesimal small for this data set). In NIOP487, total solid-phase P concentrations are lower (600– 1000 ppm) and show less variation with sediment depth. In contrast to NIOP455, there is no apparent correlation between total solid-phase P and organic carbon in NIOP487 (r^2 = 0.14). Phosphorus accumulation rates (Pacc.), in particular those of NIOP487, are mainly regulated by variations in LSR, and vary between 5 and 25 and 2 to 10 mg P cm^{-2} ky^{-1} for NIOP455 and NIOP487, respectively (Fig. 2).

NIOP cores 487 and 455 have been extensively studied to reconstruct the paleoenvironmental conditions in the Arabian Sea (den Dulk et al., 1998; Reichart et al., 1998; Schenau et al., 2002). The downcore patterns in organic carbon (C_{org}) in these cores can be correlated with sediment cores throughout the Arabian basin (Reichart et al., 2002b). These organic carbon variations have been related to changes in paleoproductivity (Shimmield, 1992; Emeis et al., 1995; Reichart et al., 1998), which is confirmed by independent geochemical (Ba, redox trace elements) and paleontological (*G. bulloides*) proxies for paleoproductivity (den Dulk et al., 1998; Reichart et al., 1998). Accordingly, the organic-rich intervals in NIOP455 and NIOP487 represent periods of increased paleoproductivity. The bottom waters of NIOP455 have periodically experienced reduced BWO concentrations as the result of changes in OMZ intensity through time. This is evidenced by the alternation of laminated intervals, and the downcore distributions of redox-sensitive elements (den Dulk et al., 1998; Reichart et al., 1998; den Dulk et al., 2000) and benthic foraminifera (den Dulk et al., 1998; den Dulk et al., 2000). The bottom waters of NIOP487, on the other hand, have remained well-oxygenated during the last

185 kyr (Schenau et al., 2002), since the OMZ has never extended to the deepest part of the Arabian Basin.

To evaluate P burial under different paleoenvironmental conditions, we have reconstructed paleoburial efficiencies for P (here defined as the fraction of the depositional P flux that is preserved upon burial). In most marine systems, reactive P is primarily delivered to the sediment as particulate organic matter (e.g., Delaney, 1998; Schenau and de Lange, 2001; see also section 3.2.2.). The particulate P flux to the seafloor can thus be estimated by calculating the paleoexport productivity of organic phosphorus (PP_{export}; gP m^{-2} y^{-1}), using the transfer function developed by Sarnthein (Sarnthein et al., 1992):

$$PP_{export} = \frac{24.16 \times C^{0.493} \times z^{0.3}/LSR_{OCF}^{0.105}}{(C/P)_{org}} \quad (1)$$

where C_A is the organic carbon accumulation rate (g m^{-2} y^{-1}), z the water depth (m), LSR_{OCF} the organic-carbon-free linear sedimentation rate (cm ky^{-1}), and $(C/P)_{org}$ the Redfield nutrient ratio of fresh organic matter (106) (Fig. 3). The phosphorus burial efficiency (PBE) can be calculated using the equation:

$$PBE(\%) = 100 \times \frac{[P] \times MAR}{10^5 \times PP_{export}} \quad (2)$$

where [P] is the total solid-phase P concentration (ppm), and MAR the mass accumulation rate (g cm^{-2} ky^{-1}) (Fig. 4). Note that this PBE is not equal to the sedimentary burial efficiency, as regeneration of particulate P occurring during transit through the water column is included. Although recently Payton et al. (2003) showed that a significant transformation from organic into inorganic phosphorus might occur in the water column, this does not influence calculation of burial efficiencies based on export productivity. In NIOP487 the estimated PBEs are generally lower during periods of increased productivity, although not distinguishable during stage 5 (Fig. 4). NIOP455 shows the same pattern, but less distinct than in NIOP487.

The PBEs calculated with Eqn. 2 are sensitive to variations in MAR. The downcore PBE distributions, therefore, show large shifts at the abrupt changes in LSR (Fig. 4). In the northern Arabian Sea, variations in sedimentation rates are largely controlled by changes in dust input, which are related to glacial-interglacial variability in continental aridity (Clemens and Prell, 1990; Sirocko, 1991). The resolution of the time frame used in this study does not allow for distinguishing MAR variability on sub-Milankovitch time scales. Periods of precession-related productivity maxima are linked to intensified summer monsoon wind strength (Clemens and Prell, 1990). Intensification of the monsoon causes more wet climate conditions and reduced dust formation. In addition, strong SW monsoonal winds suppress the northwesterly winds that carry dust from the Arabian Peninsula to the Arabian Sea (Sirocko et al., 1993). Consequently, periods of increased productivity are associated with reduced sedimentation rates. Using lower MARs for periods of high productivity in Eqn. 2 would result in an even sharper contrast in PBE between periods of high and low productivity. Sub-Milankovitch scale fluctuations in sedimentation rate thus cannot account for the calculated variations in PBE.

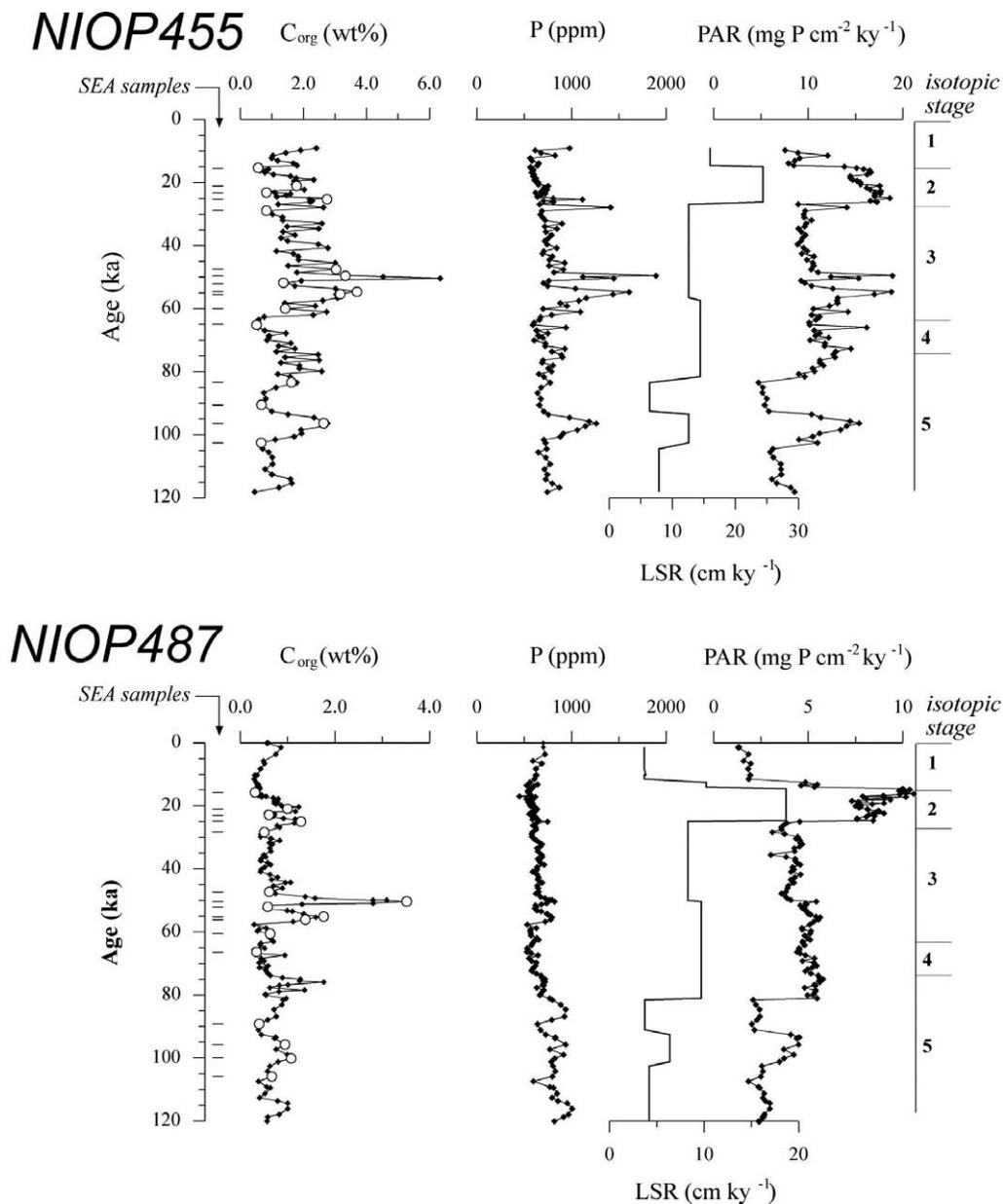Calculation of paleoexport productivity rates with Eqn. 1 is

Fig. 2. Sediment records of organic carbon (C_{org}; wt%), total solid-phase P (ppm), P accumulation rate (PAR; mg P cm^{-2} ky^{-1}), and linear sedimentation rate (LSR; cm ky^{-1}) vs. age for NIOP 455 and NIOP487. The samples selected for sequential extraction analysis (SEA; Fig. 5) are indicated by the open circles and lines at left hand side of figure. Isotopic stages are indicated at the right side.

only valid for pelagic sediments deposited in oxic environments with BWO concentrations above 50 μM (Sarnthein et al., 1992). Dysoxic bottom waters may cause enhanced preservation of organic matter, resulting in an overestimation of the PP$_{export}$ flux. This may explain the overall higher calculated PP$_{export}$ fluxes for NIOP455 compared to NIOP487 (Fig. 3). However, the PP$_{export}$ fluxes in NIOP455 are not systematically higher in the laminated intervals. To determine the potential effect of organic matter preservation in NIOP455, the PBEs were recalculated using the PP$_{export}$ fluxes calculated for NIOP487 (i.e., sediments deposited under oxic conditions), assuming that fluctuations in paleoproductivity were similar

throughout the Arabian basin (Reichart et al., 1998; Reichart et al., 2002b). The recalculated values do not significantly alter the PBE pattern (Fig. 4). Periodical preservation of organic matter therefore does not induce the lower PBEs in the organic-rich intervals of NIOP455.

The absolute values of the PBEs must be considered with caution in view of the inaccuracies included calculating PP$_{export}$ fluxes. However, the results show a distinct contrast in PBE under different paleoenvironmental conditions. In the next section, we will discuss the burial behaviour of the different P fractions, namely 1) organic P, 2) biogenic apatite, 3) P adsorbed to iron oxides and detrital apatite, and 4) authigenic
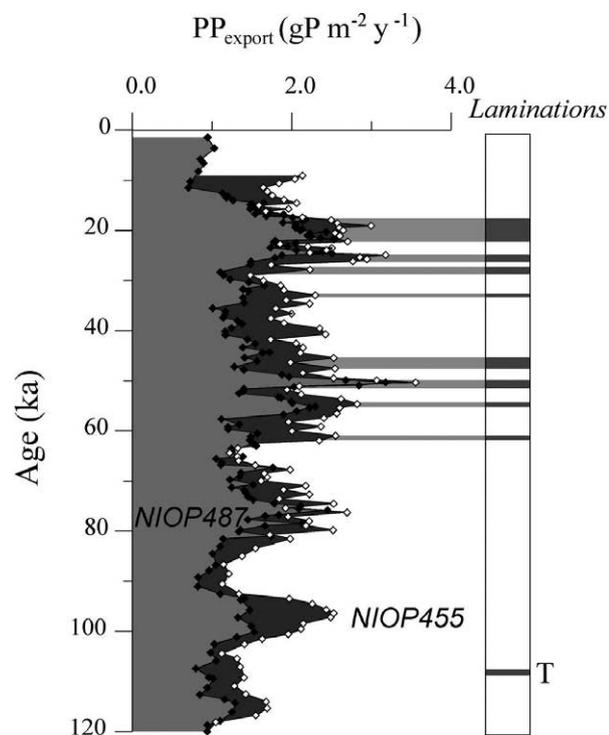
Fig. 3. Records of calculated paleoexport fluxes of particulate organic P (PP$_{export}$; gP m^{-2} y^{-1}) vs. age for NIOP455 ($\diamond$) and NIOP487 ($\blacklozenge$). The darker shaded area between the two curves represents the difference in PP$_{export}$ flux between NIOP455 and NIOP487. Laminated sediment intervals in NIOP455 are indicated at the right side of the figure. A turbiditic layer in the lower part of NIOP455 is indicated with the letter T.

apatite, to determine the processes responsible for the lower PBE during periods of increased paleoproductivity. Here we focus on precessional and sub-Milankovitch variations in paleoproductivity, since the records analyzed only span one full glacial to interglacial cycle it is not possible to generalize the discussion to longer time scales.

3.2. Sedimentary P Speciation

3.2.1. Organic phosphorus

In NIOP455 and NIOP487, organic phosphorus (P$_{org}$) constitutes only a minor P fraction relative to total solid-phase P (on average respectively 6 and 12%; Fig. 5). Organic P is thus a relatively unimportant reactive P sink in the Arabian Sea. This finding is consistent with P speciation results from other deep pelagic sediments (Lucotte et al., 1994; Filippelli and Delaney, 1996; Delaney and Anderson, 1997; Table 1). During periods of high paleoproductivity, P$_{org}$ concentrations increase in both cores (Figs. 5 and 6), which is in accordance with the higher organic matter contents (Fig. 2). In NIOP487, C$_{org}$/P$_{org}$ ratios are generally higher in the organic-rich intervals, indicating that burial of organic P relative to organic carbon is less efficient during periods of high productivity. A similar pattern is absent in NIOP455. The C$_{org}$/P$_{org}$ ratios in NIOP455 are higher (680 to 1470) than in NIOP487 (130–570).

Sedimentary C$_{org}$/P$_{org}$ ratios are usually higher than that of fresh marine planktonic organic matter (106; Redfield et al., 1963) as the result of preferential regeneration of P relative to carbon during organic matter decomposition (e.g., Suess and Muller, 1980; Mach et al., 1987; Ingall and Van Cappellen, 1990). Some workers have observed particularly elevated C$_{org}$/P$_{org}$ ratios in sediments underlying anoxic bottom water conditions (e.g., Ingall and Van Cappellen, 1990; Ingall et al., 1993), although others noted no or little difference (Colman and Holland, 2000; Anderson et al., 2001; Filippelli, 2001). The fluctuations in sedimentary C$_{org}$/P$_{org}$ ratios in NIOP487 cannot be attributed to variations in bottom water redox conditions, because the bottom waters of NIOP487 have remained well-oxygenated during the Late Quaternary. Sedimentary C$_{org}$/P$_{org}$ ratios may also be influenced by temporal admixing of terrestrial organic matter, which in comparison to marine organic matter, is depleted in P (Ingall et al., 1993). Sedimentary organic matter in the northern Arabian Sea is primarily marine in origin (Pedersen et al., 1992; van der Weijden et al., 1999; Sinninghe Damste et al., 2002). Reichart et al. (1997) found no evidence in Arabian Sea sediment records for enhanced input of terrestrial organic matter during periods of precessionally induced high productivity. Consequently, varying inputs of allochthonous organic matter cannot account for the fluctuations in the C$_{org}$/P$_{org}$ ratios found in NIOP487. The most probable explanation for the C$_{org}$/P$_{org}$ pattern in NIOP487 is different contributions of bacterial organic matter that is characterized by low C$_{org}$/P$_{org}$ ratios (~50; Reimers et al., 1990). During periods of low productivity, the organic matter deposited will be largely transformed into bacterial biomass. At higher organic matter accumulation rates, bacterial remains will be diluted with organic material deposited from the water column.

The higher C$_{org}$/P$_{org}$ ratios in continental slope core NIOP455, compared to deep pelagic core NIOP487, are probably related to the higher sedimentation rates, overall lower BWO concentrations, and relatively lower bacterial organic matter contents. C$_{org}$/P$_{org}$ ratios show no consistent response with respect to changes in paleoproductivity or BWO conditions. Apparently, past variations in BWO concentration were insufficient to substantially affect the C$_{org}$/P$_{org}$ ratio in these sediments. We conclude that organic P retention is reduced in sediments of the deep Arabian Basin during periods of increased paleoproductivity, whereas no such trend is detected for continental slope sediments.

3.2.2. Biogenic apatite

At present, the Arabian Sea sustains relatively high fish production rates (FAO, 1981). The hard parts of fish consist primarily of amorphous hydroxy apatite (Posner et al., 1984), and burial of fish debris has been recognized as a potentially important process to remove reactive P from the oceans (Suess, 1981; Schenau and De Lange, 2000). The export flux of P associated with biogenic apatite is approximately a factor 10 less than that of organic P (Schenau and De Lange, 2001). Phosphorus associated with fish debris (P$_{fish}$), however, constitutes on average the largest P fraction in NIOP455 (37%) and NIOP487 (32%; Fig. 5). This is remarkable, as fish debris are usually considered to dissolve predominantly before burial, and therefore represent an unimportant sink of reactive P (e.g.,
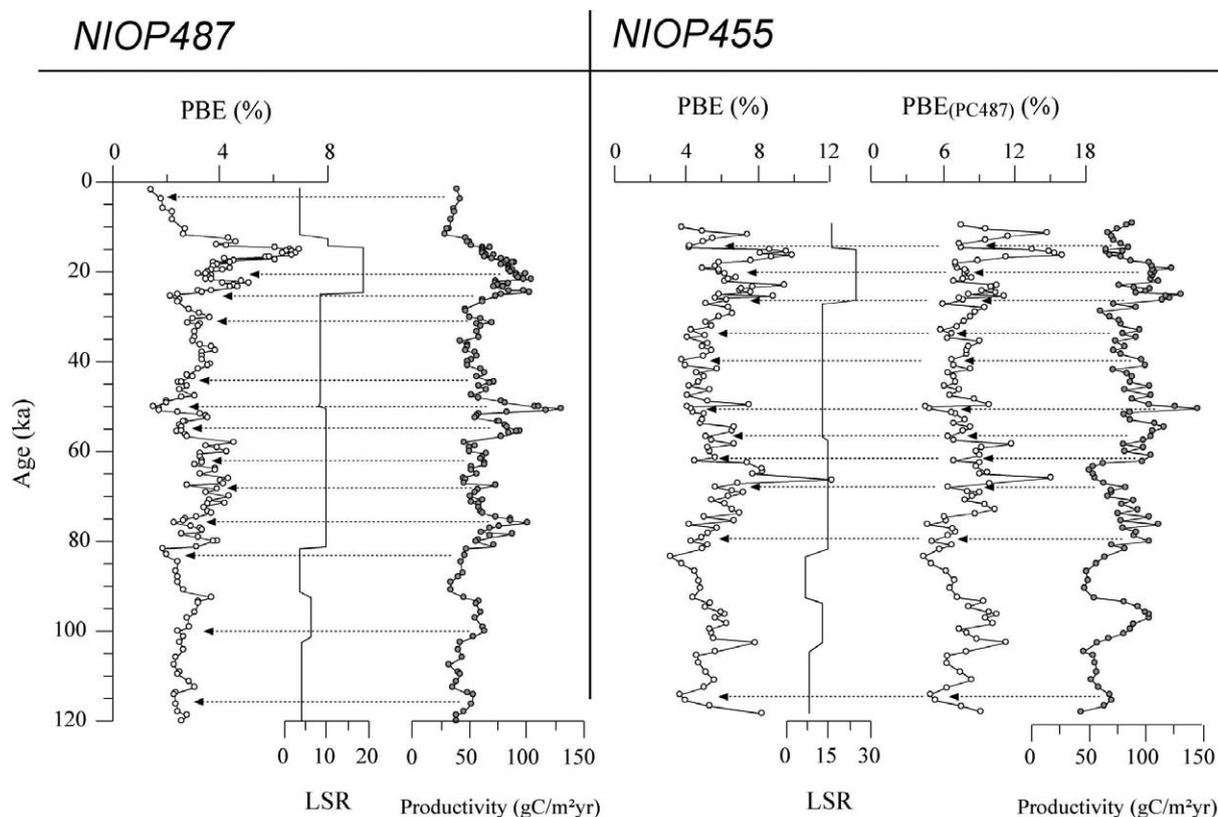
Fig. 4. Records of burial efficiencies for phosphorus (PBE) vs. age for NIOP455 and NIOP487, as calculated with Eqn. 2 (see text). The LSR has been plotted to identify the shifts in PBE related to abrupt changes of the mass accumulation rate. For NIOP455, the phosphorus burial efficiency has also been calculated using the calculated paleoexport fluxes for NIOP487 (Fig. 3) (PBE(NIOP487)). The arrows point to low PBEs during periods of reconstructed high paleoproductivity (gC/m^2yr).

Froelich et al., 1982). The accumulation of P_{fish} is ~5 times more important than the accumulation of P_{org} (Fig. 5). Consequently, P regeneration from biogenic apatite in water column and sediment is slower than that from organic matter. This may be explained by the relatively large size and high density of fish debris, which will make them sink fast to the seafloor. In addition, adsorption of fluoride occurring in water column and porewater makes biogenic apatites more resistant to dissolution (Atlas and Pytcowicz, 1977).

The P_{fish} concentration in NIOP455 is high during periods of high paleoproductivity (Fig. 6). Increased primary productivity rates induce higher fish production, resulting in higher accumulation rates of fish debris. Additionally, fish debris in this core may have been subject to preservation effects related to the periodically reduced oxygen content of bottom water and top sediment. In contrast to oxic organic matter degradation, no acidity is produced during suboxic (denitrification, Mn- and Fe-oxide reduction) and anoxic (sulphate reduction) diagenesis (provided that all H_2S is consumed by pyrite formation; Canfield and Raiswell, 1991), thereby reducing sedimentary dissolution of biogenic apatite. Furthermore, high-phosphate porewater concentrations, typical of organic rich sediments deposited from low-oxygen water columns, lead to thermodynamic supersaturation with respect to apatite (Atlas and Pytcowicz, 1977), which will decrease dissolution of fish debris. Sediments located within a dysoxic environment, therefore, may experience enhanced preservation of fish debris

(Schenau and De Lange, 2000). In contrast to NIOP455, the P_{fish} concentration in the glacial intervals of NIOP487 is not significantly enriched during periods of high paleoproductivity (Fig. 6). This may be attributed to higher regeneration rates of fish debris in the deep pelagic site relative to the more shallow continental slope sediments, as the result of a larger water depth, lower MARs, and more oxygenated bottom water conditions (Schenau and De Lange, 2000; 2001). In addition, the different food web structure of the more oligotrophic open ocean environment (Ryther, 1969), the high seasonality of primary productivity in the Arabian Sea, and the nonlinear response of transfer efficiency to food availability (Cushing, 1973) causes fish production to be less sensitive to changes in surface water productivity.

3.2.3. Detrital and iron bound P

Iron-bound P constitutes an important P fraction in surface sediments overlain by oxic bottom waters (e.g., Sundby et al., 1992; Slomp et al., 1996). In NIOP455 and NIOP487, iron-bound P contents (P_{Fe}) are low compared to the other P fractions (8.5 and 15% respectively; Fig. 5), indicating that this fraction is an unimportant reactive P sink in Arabian Sea sediments. Low P_{Fe} contents are consistent with the low reactive iron oxide contents (Fe_{CDB}) in these sediments (2000 to 4000 ppm for NIOP487 and 1000 to 2000 ppm for NIOP455). As the result of a relatively high input of reactive
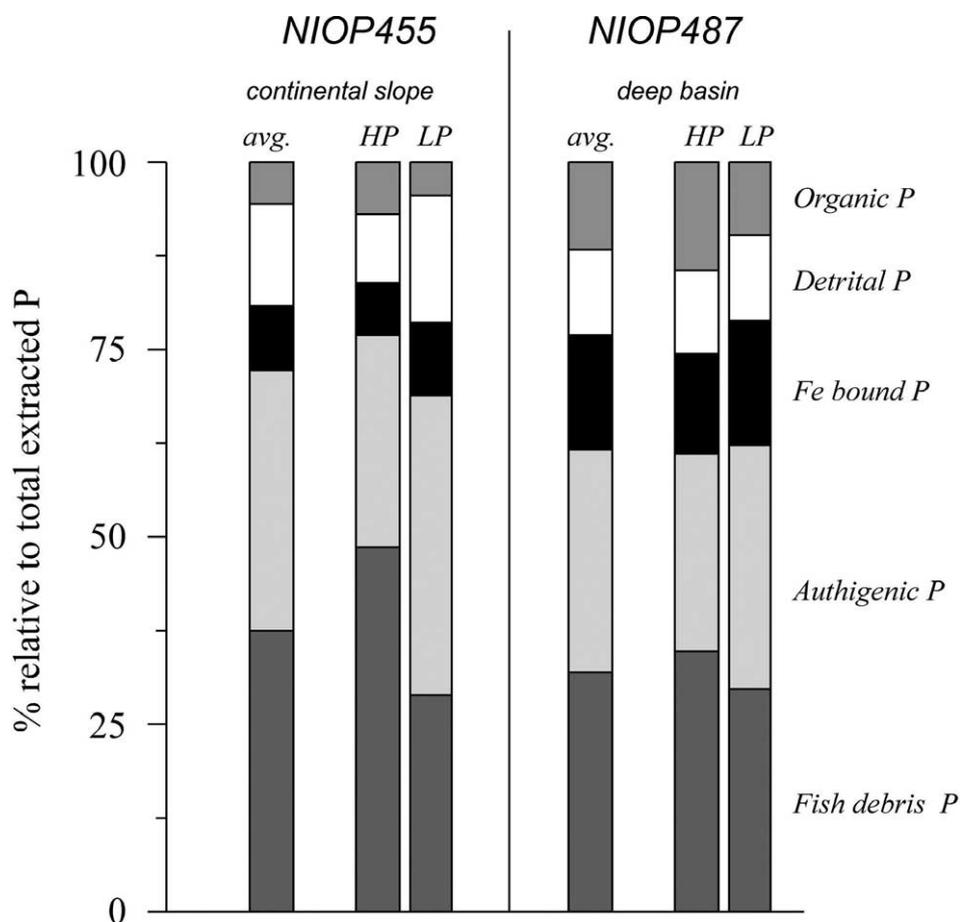
Fig. 5. The solid-phase P speciation relative to total extracted P for sediment samples from NIOP455 and NIOP487. The average P speciation for all samples (avg.), and the average P speciation for periods of high (HP) and low paleoproductivity (LP) is given.

organic matter, easily dissolvable iron oxides are reduced in the surface sediments of the continental slope (van der Weijden et al., 1999) and the deep basin (Schenau and De Lange, 2001) of the Arabian Sea during early diagenesis. The Fe_{CDB} fraction that remains below the zone of active iron oxide reduction consists of refractory iron oxides and iron extracted from the partial dissolution of clay minerals (Canfield, 1989; Rutten and de Lange, 2003). The higher Fe_{CDB} contents of NIOP487 compared to NIOP455 are probably related to more oxygenated bottom water conditions and a lower reactivity of the sedimentary organic matter. Burial of the P_{Fe} fraction in both cores is not affected by changes in paleoproductivity and/or BWO concentration (Fig. 6). Apparently, also during periods of reduced organic carbon accumulation sufficient reactive organic matter is present to ensure reduction of all easily reducible iron oxides.

Nonreactive detrital apatite (P_{det}) is a small and rather constant P fraction in each core (Figs. 5 and 6). The contribution of the nonreactive fraction, therefore, will not significantly influence the calculated PBEs. The higher P_{det} concentrations in NIOP455 are probably related to the higher content of terrigenous material.

3.2.4. Authigenic apatite

Authigenic carbonate fluoroapatite (CFA) is a relatively important sink of reactive P in the sediments of this study (P_{CFA}; Fig. 5). Interestingly, the average P_{CFA} fraction in the deep basin and continental slope core is of the same order of magnitude (35 and 29% for NIOP455 and NIOP487, respectively). The P_{CFA} concentrations do not increase during periods of higher productivity (Fig. 6). Higher reactive P deposition rates apparently do not automatically induce higher rates of *in situ* authigenic CFA formation.

Potentially, diagenetic redistribution of P may substantially have altered the downward distribution of solid-phase P (Lucotte et al., 1994): phosphate liberated in intervals initially enriched in P diffuses away to precipitate as CFA outside these intervals. Authigenic apatite formation occurs principally in the surface sediment in the Arabian Sea, in both the deep Arabian basin and on the continental slope (Schenau and De Lange, 2001). The proportion of P_{CFA} does not increase with sediment depth, as has been observed in Ocean Drilling Program (ODP) cores that cover timescales up to 65 Ma (Filippelli and Delaney, 1996; Anderson et al., 2001). Apparently, a gradual conversion of organic P into CFA does not occur on the timescales studied here. The impact of early diagenetic redistribution can be

Table 1. Partitioning of reactive P in sediments of the continental margin (Ruttenberg and Berner, 1993), the deep Pacific ocean (Filippelli and Delaney, 1996), and the Arabian Sea (this study), and estimates for the global average.

Reactive P sinks	Continental margin[1]	Pacific Ocean[2]	Arabian Sea[3]	Estimated global average		
				Froelich (1982)	Ruttenberg (1993)	This study
Organic P	22%	6%	10%	40%	22%	16%
Iron-P	16%	11%	12%	11%	22%	14%
Loosely sorbed-P	7%	5%	} 40%[4]	—	7%	} 35.5%[4]
Carbonate-P	} 55%	} 78%		40%	} 49%	
Fish-P				<2%		
Authigenic-P			38%	<10%		34.5%

Note that the P speciation (organic P, iron bound P, and biogenic authigenic P fractions) in deep Pacific Ocean and Arabian Sea sediments is similar. The global average for the reactive P partitioning in marine sediments was estimated using the results for the continental margin (Ruttenberg, 1993; second column) and the Arabian Sea (deep-pelagic sediment; fourth column), assuming that the total annual sedimentary burial of reactive P in deep pelagic sediments is of the same magnitude as that in continental shelf areas (Froelich, 1984; Follmi, 1996). The P fraction associated with biogenic apatite for continental margin sediments is assumed to constitute half the authigenic P pool (likewise Arabian Sea sediments). Comparison with previous estimates (Froelich et al., 1982; Ruttenberg and Berner, 1993) indicates that burial of authigenic and biogenic apatite fraction is relatively more important than previously assumed, whereas organic P burial is of secondary importance.

[1] Ruttenberg (1993).
[2] Filippelli and Delaney (1996).
[3] Average from NIOP455 and NIOP487.
[4] Primarily consisting of P associated with biogenic apatite (fish debris).

determined by examining the downcore P distribution over longer (i.e., precessional) time intervals, because this process will transport phosphate only over relatively short distances. Since the number of data points is rather limited, we calculated average C_{org}/P_{reac} ratios for precessional induced periods of high and low productivity (Fig. 7). Reactive P (P_{reac}) is here defined as all solid-phase P that may be potentially regenerated to the water column, which is equal to the total solid-phase P concentration minus the detrital P concentration. The detrital P concentration was taken as a fixed amount (see section 3.2.3). C_{org}/P_{reac} ratio gives an indication for the relation between input and burial of P but is not affected by the abrupt shifts in LSR. For both cores, average C_{org}/P_{reac} ratios for precessional induced periods of increased productivity are consistently higher than for the intermediate intervals. We argue that post-depositional redistribution has only a limited effect on reshaping the downcore distributions of solid-phase P.

Several processes may explain the lack of response of P_{CFA} burial to changes in paleoproductivity. Firstly, an increase of the reactive P deposition flux may principally lead to more P regeneration and loss to the water column. This is particularly true for the deep pelagic sediments of the Arabian Sea, where the large water depth, oxic bottom waters, and relatively low sedimentation rates cause reactive P regeneration to take place, chiefly in the water column and at the sediment water interface (Schenau and De Lange, 2001). A higher input of P, thus, will lead to burial of more refractory (bacterial) organic matter (as is indicated by the lower C_{org}/P_{org} ratios in NIOP487). Secondly, authigenic CFA formation may be regulated by diagenetic iron cycling (Sundby et al., 1992; Slomp et al., 1996). During periods of low paleoproductivity, this mechanism is more efficient in promoting authigenic CFA formation, because a reduced supply of reactive organic matter will increase the oxygen penetration depth, and thus, the sorption capacity of the

iron oxides for phosphate (Sundby et al., 1992; McManus et al., 1997). Presently, however, diagenetic iron cycling does not promote CFA formation in the deep Arabian Basin due to the refractory nature of the deposited organic matter (Schenau and De Lange, 2001). Thirdly, CFA formation rates may depend on other parameters, such as the downward diffusion rate of fluoride from the bottom water, precipitation kinetics, the permeability of the sediment, or microbial mediation (e.g., Filippelli and Delaney, 1994; Krajewski et al., 1994). Fourthly, downward mixing (i.e., bioturbation) of solid-phase reactive P may be essential to prevent direct loss of phosphate to the bottom water and to produce high-subsurface phosphate concentrations (Schenau et al., 2000). Accordingly, authigenic CFA formation rates may have been relatively reduced in the laminated intervals of NIOP455.

3.3. Cause and Implications of Reduced PBE During Periods of High Productivity

Close inspection of the solid-phase P speciation reveals that four processes may account for the reduced PBE observed during periods of high productivity in the Arabian Sea. Firstly, diagenetic redistribution may have changed the primary downcore distribution of sedimentary P, but as discussed, this process has had only a limited effect on the calculated PBEs. Secondly, the export and burial flux of reactive P are largely decoupled. Whereas P is predominantly removed from the oceans as particulate organic P, this phase constitutes only a minor fraction in the underlying sediments compared to biogenic apatite (Fig. 5; see also Table 1). Higher authigenic P formation may, in addition, have been fueled by dissolution of fish debris instead of organic matter degradation (Schenau et al., 2000). Burial of biogenic apatite, rather than organic P, is thus a more important mechanism to remove reactive P from
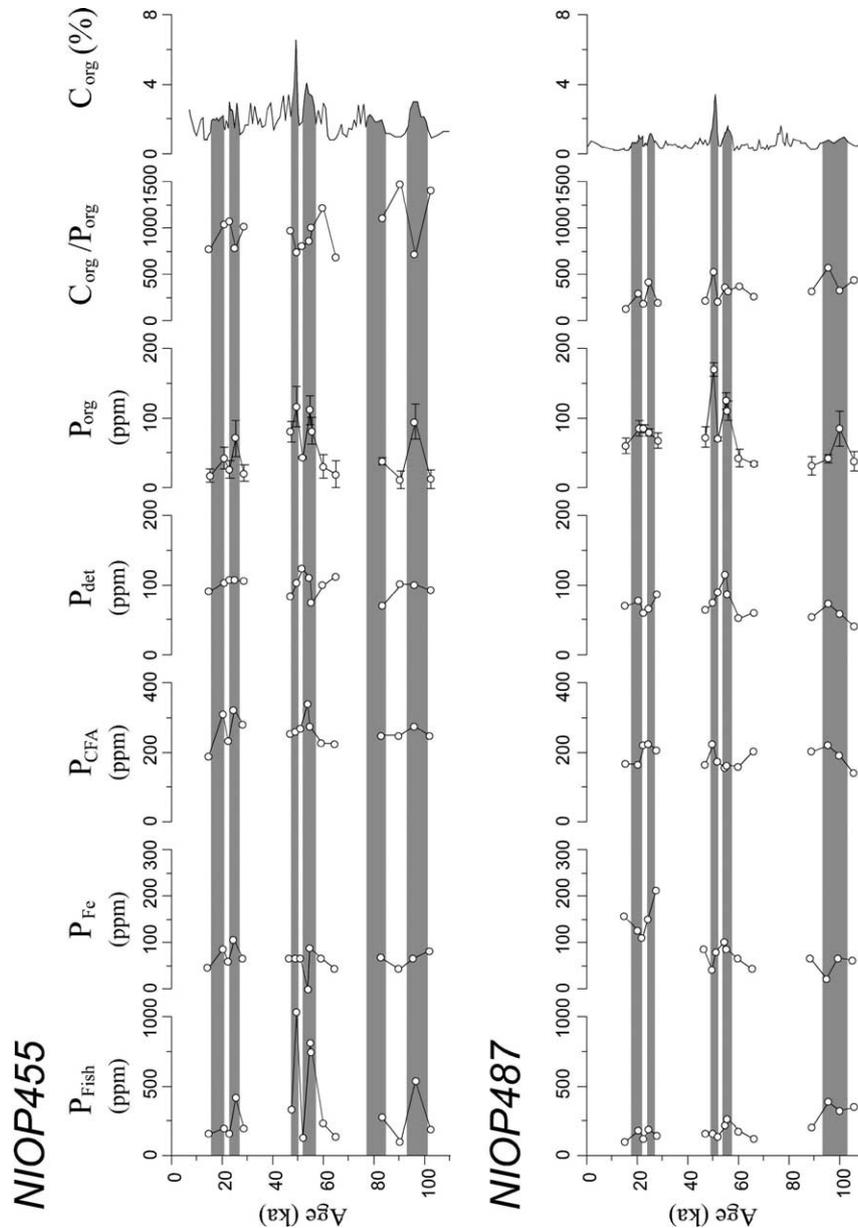
Fig. 6. Records of solid-phase P speciation (ppm) and C_{org}/P_{org} ratios vs. age for one interglacial and two glacial intervals from NIOP455 and NIOP487: P associated with fish debris (P_{fish}), iron bound P (P_{Fe}), authigenic P (P_{CFA}), P associated with detrital apatite (P_{det}), and organic P. At the right side of the figure, organic carbon records are plotted to identify intervals deposited during periods of high paleoproductivity. The error bars for organic P indicate relative errors for duplicate measurements.

the Arabian Sea. This is also evidenced by the sedimentary C_{org}/P_{reac} ratios in NIOP487 and NIOP455, which are lower than Redfield ratio for marine organic matter (106; Fig. 7). For deep pelagic sediments, P_{fish} burial does not react proportionally to changes in paleoproductivity. Consequently, burial of reactive P becomes insensitive to productivity controlled changes in P fluxes to the seafloor. This decoupling is less effective for continental slope sediments, which explains why the pattern in PBE for NIOP455 is less distinct than for NIOP487 (Fig. 4). Thirdly, authigenic P formation rates are not susceptible to changes in the rain rate of reactive P. Fourthly, more extensive P regeneration under oxygen depleted bottom

waters may have reduced P burial in continental slope sediments of the Arabian Sea during periods of intensified OMZ (Ingall and Jahnke, 1994; Ingall and Jahnke, 1997; Tamburini et al., 2003). Assessing the exact role of bottom water redox conditions on P burial in marine environments is problematic since periods of high productivity are often accompanied by bottom water anoxia. In addition, burial of the various reactive P fractions reacts differently to changes in BWO conditions. Retention of organic P is generally less efficient in sediments underlying anoxic bottom waters (Ingall et al., 1993). The limited number of sequentially extracted samples does not allow a detailed assessment of the role of past variations in
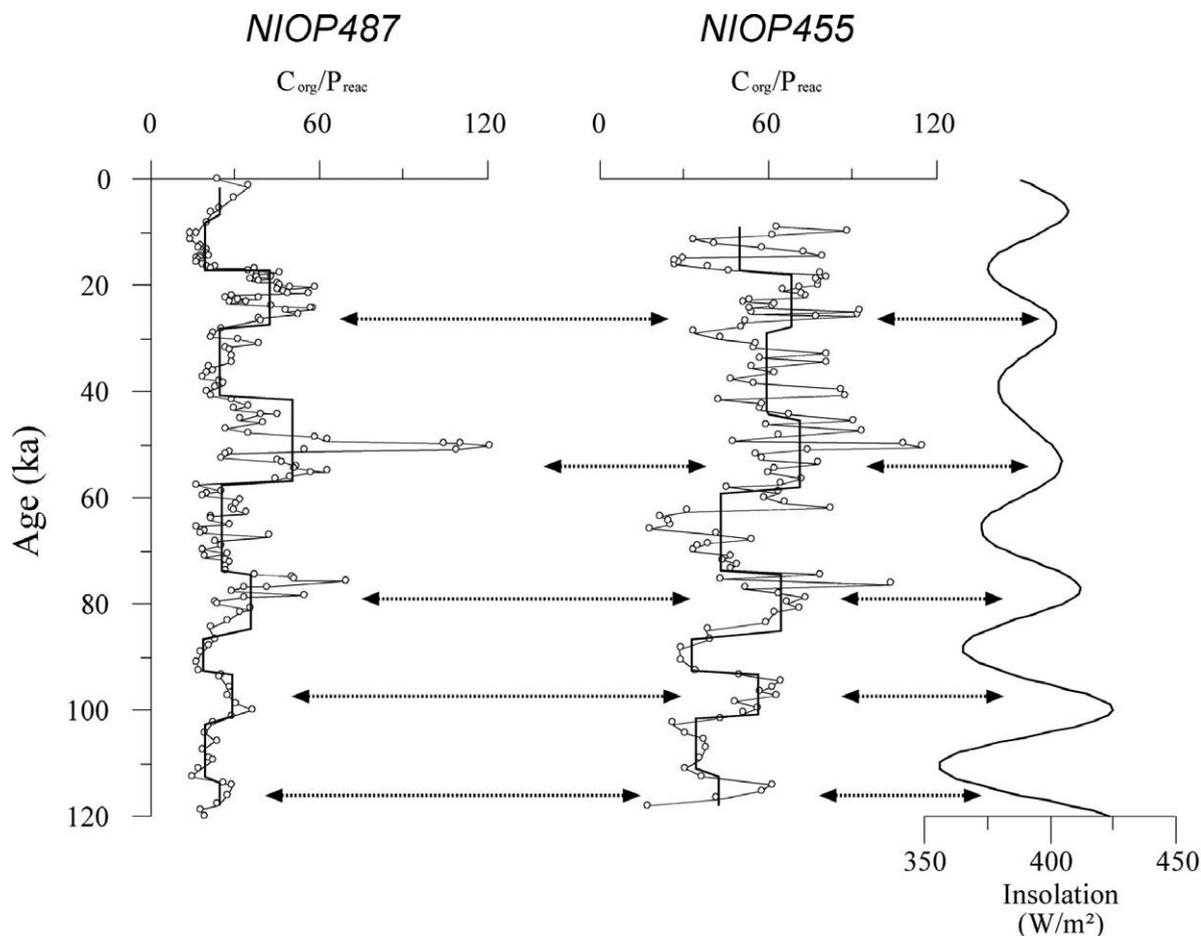
Fig. 7. Records of the C_{org}/P_{reac} ratios for NIOP455 and NIOP487 vs. age. The solid lines represent average C_{org}/P_{reac} ratios over precessional periods of high and low productivity. The 35°N September insolation curve on the right (Laskar et al., 1993) clearly shows the dominant precession cycle.

OMZ intensity on P_{org} burial. However, the potential impact of this process on the PBE is limited, as P_{org} constitutes only a minor sedimentary P fraction. In contrast to organic P, fish debris may have been subject to enhanced preservation during periods of bottom water anoxia, resulting in more efficient P burial. Finally, dysoxic bottom water conditions may either enhance (higher organic P and fish debris contents, reduced phosphate loss to the bottom water by bioturbation) or reduce (no or less efficient early diagenetic iron cycling, reduced downward mixing of sources by bioturbation) CFA precipitation rates. Fluctuating BWO contents have certainly influenced the quantity and quality of P burial in continental slope sediments of the Arabian Sea, but the precise impact on the PBE remains unclear.

Lower PBEs during periods of increased paleoproductivity imply more effective reactive P regeneration. When the regenerated phosphate is transferred back to the surface waters, it may stimulate higher rates of primary productivity (provided that phosphate is the bio-limiting nutrient). Increased surface water productivity, in turn, will increase the export flux of reactive P. Accordingly, a positive feedback loop is created between increased surface water productivity and enhanced P cycling. A similar feedback mechanism has previously been proposed for P cycling and water col-

umn anoxia (Ingall and Jahnke, 1994; Ingall and Jahnke, 1997). The results of the present study, however, indicate that an increase in productivity "automatically" induces a positive feedback, irrespective of whether or not higher organic matter accumulation rates cause oxygen depletion of the bottom waters. This conclusion has important implications for the assessment of the global cycle of P and its potential control on marine productivity and organic carbon burial.

A positive feedback between enhanced phosphorus regeneration and higher primary productivity can only be effective on time scales equal to or larger than the oceanic residence time of phosphate (Van Cappellen and Ingall, 1994). Estimates for the oceanic residence time of phosphate vary between 10 and 38 kyr (Ruttenberg, 1993; Van Cappellen and Ingall, 1994; Colman and Holland, 2000). Consequently, a positive feedback may be operative on precessional or sub-Milankovitch scale variations in paleoproductivity in the Arabian Sea. Recently, a regeneration-productivity feedback has been invoked to explain precessional-scale productivity variations in the Mediterranean (Slomp et al., 2002; Filippelli et al., 2003). In the present-day situation all regenerated phosphate released from deep basin sediments in the Arabian Sea is taken up in the Antarctic bottom waters and is transported out of the Arabian Sea. Changes in P burial will thus not directly influ-

ence primary productivity in the basin itself. On the Oman and Somalian margins, however, upwelling waters originating from intermediate water depths provide a possible way to transfer phosphate more rapidly to the photic zone. The generally higher PBEs during the glacial period indicate less efficient P cycling and lower seawater phosphate concentrations. This is consistent with Cd/Ca and $\delta^{13}C$ data from the Arabian Sea, indicating more nutrient depleted conditions during the last glacial maximum (Boyle et al., 1995), and is in accordance with the overall lower paleoproductivity rates compared to the interglacial periods (Emeis et al., 1995). During the Late Quaternary, sub-Milankovitch variations in paleo-productivity in the Arabian Sea may thus partly be regulated by changes in P burial.

4. CONCLUSIONS

The average solid-phase P speciation is very similar for continental slope and deep marine sediments of the Arabian Sea. Authigenic and biogenic apatite (fish debris) make up the bulk of the P inventory (ca. 70%), whereas P associated with iron oxides, organic P, and detrital apatite constitute only minor fractions. The concentrations of all sedimentary P species generally do not increase during periods of high paleo-productivity, with exception of organic P, and for continental slope sediments, the P fraction associated with fish debris.

The phosphorus burial efficiency (PBE) decreases during periods of increased paleoproductivity in deep marine, and although less pronounced, in continental slope sediments of the Arabian Sea. Lower PBEs during periods of higher paleoproductivity are explained by (a) the partial decoupling of the P export flux, consisting primarily of particulate organic P, and the P burial flux, consisting primarily of biogenic and authigenic apatite, and (b) the lack of higher rates of authigenic CFA formation during periods of increased reactive P deposition. Fluctuations in bottom water oxygen content may have affected P burial on the continental slope sediments of the Arabian Sea, but the precise impact on the PBE remains unclear. The results of this study indicate that a higher oceanic primary productivity induces more efficient P cycling in the oceans. Over geological time scales, this process may stimulate higher surface water productivity (assuming that P is the ultimate bio-limiting nutrient in the oceans), thus creating a positive feedback loop. In the Arabian Sea, such a feedback mechanism may also be active on sub-Milankovitch time scales, as P regenerated on the continental slopes of the Oman and Somalian coastal upwelling areas is transported to the photic zone relatively fast.

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