

A novel chemical method to quantify fish debris in marine sediments

S. J. Schenau¹ and G. J. De Lange

Department of Geochemistry, Institute of Earth Sciences, Utrecht University, Budapestlaan 4, 3584 CD Utrecht, The Netherlands

Abstract

Burial of fish bones, which consist primarily of hydroxyapatite, has been recognized as a mechanism to remove reactive phosphorus from the oceans. In this study, a new method is presented, which differentiates P associated with biogenous apatite (P_{fish}) from other P fractions. The method, consisting of a sequential chemical extraction with 2 M NH_4Cl , has been successfully tested on standard materials. It enables us, for the first time, to quantify fish debris in sediment records and to assess their importance for the marine phosphorus cycle.

The NH_4Cl extraction has been applied to sediment samples from the Arabian Sea. Preservation of fish debris is significantly higher in sediments located above 1,200 m water depth than it is for deeper sediments. The distribution of P_{fish} contents in surface sediments is predominantly governed by the extent of fish debris regeneration, which is related to differences in water depth and sedimentation rates. In addition, a good correlation between high sedimentary P_{fish} contents and low oxygen bottom water concentrations suggests that the presence of the intense oxygen minimum zone may account for the enhanced preservation of fish debris in continental slope sediments.

Hard parts of marine fish (scales, bones, teeth) consist of 60–70% hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) crystals, which are embedded in an organic matrix largely composed of the fibrous protein collagen (Posner et al. 1984; Newesly 1989; Nemliher et al. 1997). In addition, many marine invertebrates, such as cestods, inarticulate brachiopods, bivalves, and gastropods, incorporate phosphate in their hard parts (Lowenstam 1972). Large reactive surface areas, as well as crystal imperfections, make biogenic hydroxyapatite more soluble than well crystallized stoichiometric hydroxyapatite, which in turn is more soluble than fluorapatite (Posner et al. 1984). Seawater is undersaturated with respect to biogenous apatite (Arrhenius 1963; Atlas and Pytkowicz 1977). As a consequence, fish debris is subject to dissolution in the water column and in the upper part of the sediment. Fish bones may also be converted into the more stable carbonate fluorapatite (CFA; Atlas and Pytkowicz 1977; Newesly 1989), through substitution of hydroxyl ions by fluoride. Part of the fish debris will ultimately be buried in the sediments. Fossil fish fragments have been found in geological deposits dating from the Early Paleozoic till the Present (e.g., Schmitz et al. 1991; Trappe 1998).

Fish debris is found in high concentrations in sediments underlying areas of coastal upwelling (Diester-Haas 1978; DeVries and Percy 1982). In these environments, dissolu-

tion of fish debris in the sediment may play an important role in regulating benthic porewater phosphate fluxes and authigenic apatite formation (Suess 1981; Van Cappellen and Berner 1988). Furthermore, burial of biogenic apatites has been recognized as a potentially important mechanism for reactive P removal in these areas (Suess 1981). However, on a global scale burial of biogenic apatites is generally considered to be an insignificant sink of reactive phosphorus compared to the other sedimentary P fractions (Froelich et al. 1982; Berner et al. 1993). Unfortunately, studies on fish debris in marine sediments are relatively scarce. Up to now, laborious handpicking was the only method to semi-quantify their presence (Suess 1981; DeVries and Percy 1982). Chemical extraction methods for phosphorus were not able to differentiate between biogenic and authigenic apatites (e.g., Ruttenger 1992).

In this study, we present a chemical extraction method, which for the first time, enables the separation of P associated with biogenic apatite (fish debris) from other sedimentary P fractions. This extraction method has been applied to sediment samples from the Arabian Sea. Here, we will concentrate on the application and results of the extraction of biogenic apatite, while detailed results of the other extraction steps are presented elsewhere (Schenau 1999). The distribution and burial potential of fish debris in sediments will be discussed in relation to fish production and regeneration processes.

Materials and methods

Sample locations—During the Netherlands Indian Ocean program (NIOP) in 1992, sediment cores were taken in the northern Arabian Sea. For this study, we selected 11 boxcores located on the Pakistan continental slope (St 451, 452, 453, 454, 455), the Murray Ridge (St 463, 464), and the Arabian Basin (St 458, 460, 466, and 487; Fig. 1, Table 1). In addition, sediment samples were used from two pistoncores (PC455 and PC455). The sample locations of these pistoncores correspond with their respective boxcores posi-

¹ Corresponding author (sjoerds@geo.uu.nl).

Acknowledgments

The chief scientists on the Netherlands Indian Ocean Programme (NIOP) cruises were W. J. M. van der Linden and C. H. van der Weijden. H. de Waard and G. Nobbe are thanked for their contribution to the laboratory analyses, and G. J. van het Veld and G. Ittman for processing the micropaleontological samples. G. J. Reichert is thanked for his assistance in the microscopical identification of fish debris. Critical reviews by C. H. van der Weijden, C. P. Slomp, A. Rutten, and two anonymous reviewers significantly improved this manuscript. This research was funded by the Netherlands Organisation for Scientific Research (NWO). This is publication 2000103 of the Netherlands School of Sedimentary Geology.

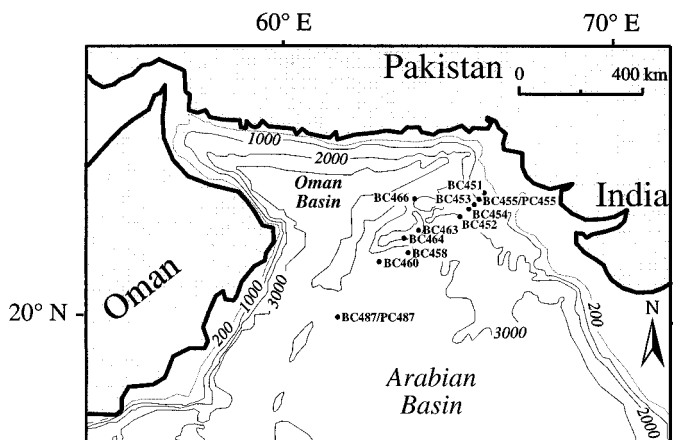


Fig. 1. Sample locations in the northern Arabian Sea of the boxcores and pistoncores used in this study.

tions (Fig. 1). Bottom water oxygen (BWO) concentrations were derived from oxygen measurements at near-by conductivity-temperature-depth (CTD)-stations (Table 1). AMS ^{14}C dating of handpicked foraminifers from the base of the boxcores (Van der Weijden et al. 1999) was used to calculate the sedimentation rates (Table 1). Mass accumulation rates (MARs) were calculated by multiplying the sedimentation rate with the dry bulk density.

Solid-phase analysis—The dry bulk density of the sediment samples was calculated from measurements of weight loss of fixed volume samples after freeze-drying. Subsequently, samples were powdered in an agate mortar to $<50\ \mu\text{m}$, and after homogenization, subsamples were taken for geochemical analyses. Bulk concentrations of P were determined by total digestion of 250 mg sample at 90°C in a 5 ml 6.5:2.5:1 mixture of HClO_4 (60%), HNO_3 (65%) and H_2O , and 5 ml HF (40%). After evaporation of the solutions at 190°C on a sand bath, the dry residue was dissolved in 25 ml 1 M HCl. The resulting solutions were analyzed with a Perkin Elmer Optima 3000 inductively coupled plasma atomic emission spectrometer (ICP-AES). All results were monitored using international (SO1, SO3) and in-house standards. Relative errors for duplicate measurements were low-

er than 3%. After removal of all carbonates with 1 M HCl, organic carbon contents (C_{org}) were measured with a Fisons NA 1500 NCS (nitrogen, carbon, sulfur) analyzer. Relative errors were less than 1%.

Sequential extraction analysis—The solid-phase speciation of phosphorus in the top 0–2 cm was examined using a 5-step sequential extraction scheme (for details see Table 2). Approximately 125 mg of dried and ground sediment was washed sequentially with (1) 25 ml 2 M NH_4Cl , pH = 7 (repeated 8 times), (2) 25 ml citrate dithionite buffer (CDB), pH = 7.6, (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 step two, three, and four, the sediment was rinsed successively with 2 M NH_4Cl (pH = 7) and demineralized water to prevent readsorption of phosphate. This extraction scheme is a modification of the SEDEX method developed by Ruttenberg (1992). The 2 M NH_4Cl extraction (step 1), which has previously been applied to extract carbonate-associated P (De Lange 1992), was included here to determine P associated with biogenic apatite (results reported in this study). All extracted solutions were measured by ICP-AES. The specificity and efficiency of each extraction step was tested by the extraction of standards, namely fish debris (vertebrae from a freshly killed whiting), ferromanganese nodule (iron-bound phosphate; collected from the Madeira Abyssal Plain), phosphorite nodule (authigenic apatite; collected from the Peru Continental Margin), and detrital apatite (in-house mineral collection). These standards were first powdered in a wolfram carbide swing-mill (grainsize $<73\ \mu\text{m}$), except for the fish debris, which were powdered manually in an agate mortar to $<50\ \mu\text{m}$. Relative errors of P for duplicate samples for each extraction step are given in Table 2. For sediment samples, recovery for P with respect to total P was approximately 90%.

Fish debris and foraminiferal analyses—Sediments were sieved into three fractions (65–150 μm , 150–595 μm , $>595\ \mu\text{m}$) in order to determine the distribution of fish debris over the different sediment fractions. For all boxcore samples, fish debris was quantified in the 150–595 μm fraction under a microscope by counting the number of fish fragments in

Table 1. Location, water depth, present oxygen concentrations of the bottom water, mass accumulation rates, C_{org} and P_{fish} concentrations in the top 2 cm of the boxcores used in this study. The boxcores located inside the OMZ ($\text{O}_2 < 10\ \mu\text{M}$) are italic.

	Latitude (N)	Longitude (E)	Water depth (m)	O_2 bottom (μM)	MAR ($\text{g cm}^{-2}\ \text{kyr}^{-1}$)	C_{org} (wt%)	P_{fish} top 2 cm (ppm)
BC451	23°41'4	66°02'9	495	<2	12.5	4.09	382
BC452	22°56'4	65°28'1	2001	87.1	3.8	1.07	158
BC453	23°14'0	65°44'0	1555	39.3	5.6	1.23	157
BC454	23°26'9	65°51'2	1254	12.5	6.0	3.36	189
BC455	23°33'3	65°57'2	998	<2	6.8	4.28	320
BC458	21°59'7	63°48'8	3000	123.7	4.0	0.76	145
BC460	21°43'2	62°55'2	3262	125.3	—	0.86	205
BC463	22°33'6	64°03'3	970	<2	5.2	5.67	310
BC464	22°15'0	63°34'7	1511	34.8	4.3	1.26	179
BC466	23°36'1	63°48'5	1960	75.4	5.9	0.89	143
BC487	19°54'8	61°43'3	3566	151.0	1.9	0.80	194

Table 2. Details of the sequential extraction scheme, the extracted P fractions, and relative errors for duplicate measurements.

Step	Extractant	P phase extracted	Relative errors (%)	Reference
1	<ul style="list-style-type: none"> • 8 × 25 ml 2 M NH₄Cl (brought to pH 7 with ammonia), 4 h, 20°C 	<ul style="list-style-type: none"> • Exchangeable or loosely sorbed P • Carbonate associated P • Biogenic apatite 	<4	This study
2	<ul style="list-style-type: none"> • 1 × 25 ml 0.15 M Na-citrate, 0.5 M Na-HCO₃ (pH 7.6), and 1.125 g Na-dithionite, 16 h, 20°C • 1 × 25 ml 2 M NH₄Cl (pH 7), 2 h. • 1 × 25 ml demin. water, 2h. 	<ul style="list-style-type: none"> • Easily reducible or reactive iron-bound P 	<10	After Ruttenberg 1992
3	<ul style="list-style-type: none"> • 1 × 25 ml 1 M Na-acetate buffered at pH 4 with acetic acid, 16 h, 20°C • 1 × 25 ml 2 M NH₄Cl (pH 7), 2 h • 1 × 25 ml demin. water, 2 h 	<ul style="list-style-type: none"> • Authigenic apatite 	<10	After Ruttenberg 1992
4	<ul style="list-style-type: none"> • 25 ml 1 M HCl, 16 h, 20°C • 1 × 25 ml demin. water, 2 h 	<ul style="list-style-type: none"> • Detrital apatite 	<7	Ruttenberg 1992
5	<ul style="list-style-type: none"> • 5 ml of a 6.5 : 2.5 : 1 mixture of HClO₄ (60%), HNO₃ (65%) and H₂O, and 5 ml HF (40%), 16 h, 90°C (total digestion) 	<ul style="list-style-type: none"> • Organic P • P adsorbed to clay minerals 	<10	Lord 1982

splits (using an Otto microsplitter). Fish particles could not be adequately identified optically in the 65–150 μm fraction of sediment samples. Therefore, the chemical composition of the 65–150 μm fraction for some pistoncore samples was measured by dissolving split samples of this fraction in 1 M

HCl and analyzing them subsequently with ICP-AES. The total P content of this fraction is a measure of the fish debris content of the sample (*see discussion*).

Results and discussion

The NH₄Cl extraction: Differentiation between biogenic and authigenic apatite—Extraction results on fresh fish debris indicate that hard parts of fish are highly soluble in 2 M NH₄Cl; approximately 80% of the total amount of P present in fish debris dissolves in this step (8×) (Fig. 2). The remaining P fraction of fish debris, which is extracted during steps 2 and 3, may result from incomplete dissolution in step 1 caused by saturation of the extraction fluid or the presence of P associated with less easily dissolvable fractions in fish bones. In contrast, only small percentages of authigenic apatite, detrital apatite, and iron-bound P are extracted in NH₄Cl (Fig. 2). The higher solubility of fish bone apatite relative to authigenic apatite may be explained by (Posner et al. 1984; Newsly 1989): (a) the relative higher solubility of hydroxyapatite relative to fluorapatite, (b) the lack of crystal and chemical perfection of bone apatite, and (c) the larger surface area of biogenous apatite. Consequently, the sedimentary P fraction extractable in NH₄Cl (from here on denoted as P_{fish}) is probably primarily associated with biogenic apatite. To further substantiate this observation, a separate sequential extraction was done on sediment and standard samples, analyzing each of eight NH₄Cl steps separately (Fig. 3). For the two sediment samples (BC455, 0–2 cm; and PC487, 329 cm), the P concentration starts to increase once the Ca concentration in solution has dropped (Fig. 3A), indicating that the P fraction associated with P_{fish} begins to dissolve once all Ca-carbonates have been extracted. The Ca-carbonate content of a sample thus determines in which NH₄Cl step in the P_{fish} fraction is extracted. Consequently, the P_{fish} fraction must be associated with a Ca containing

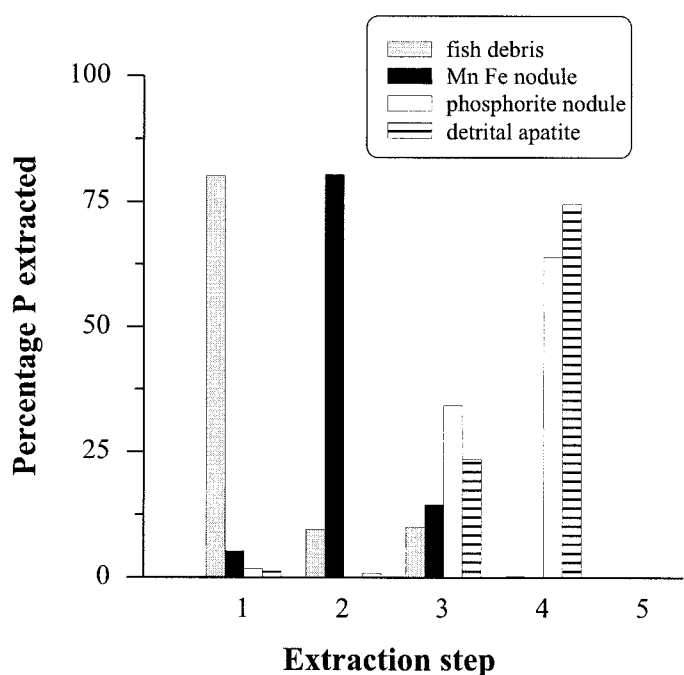


Fig. 2. Percentage of P extracted for standard materials using the extraction schedule of Table 2; each step is given relative to the total extracted P for that standard. Standards used are fresh fish debris, Mn-Fe nodule, phosphorite nodule, and detrital apatite (in-house collection). Sample weights were ca. 50 mg. The relative low P recovery for the phosphorite nodule in step 3 can be attributed to saturation of the solvent due to a relatively high solid/liquid ratio.

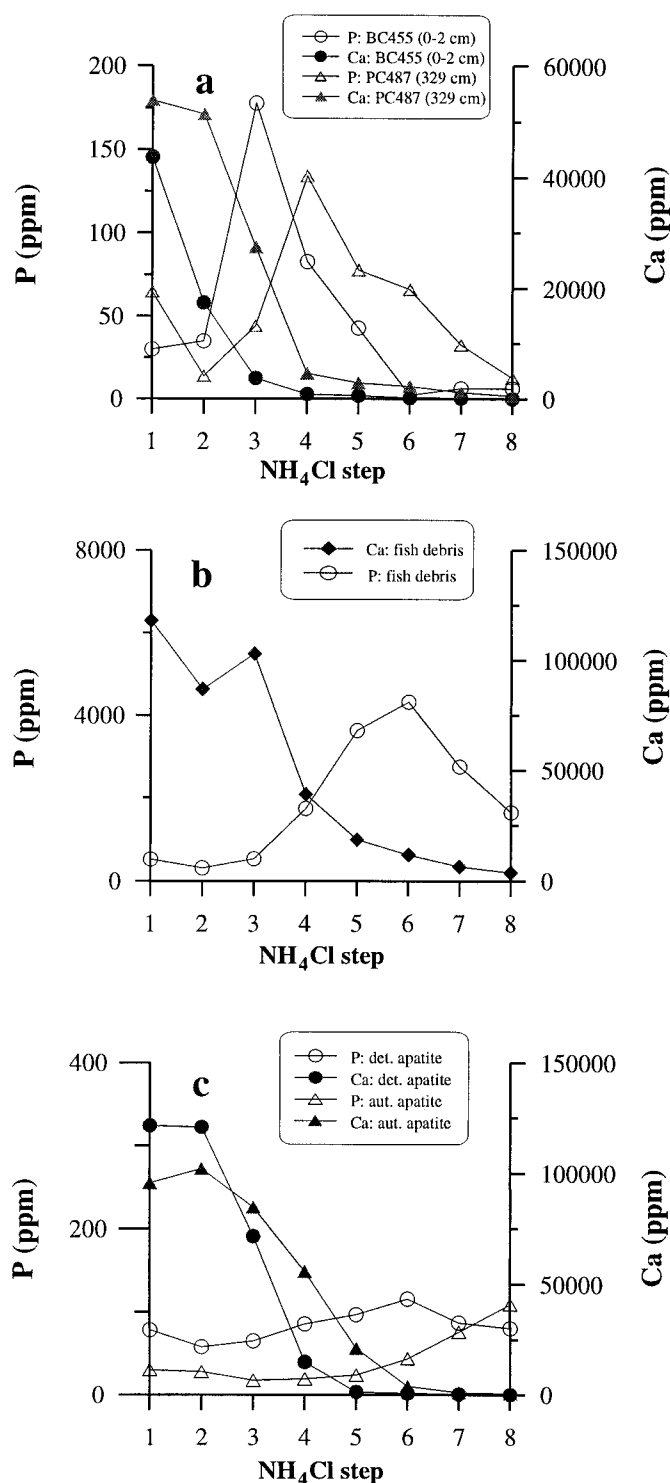


Fig. 3. Extracted P and Ca concentrations (ppm) in each step of a 8-fold 2 M NH₄Cl sequential extraction for a) two sediment samples (BC455, 0–2 cm depth; PC487, 329 cm depth; ca. 125 mg), b) a sample consisting of calcite (ca. 50 mg) and fish debris (ca. 10 mg), and c) samples consisting of calcite (ca. 50 mg) and respectively detrital (ca. 10 mg) and authigenic apatite (ca. 10 mg).

phosphate mineral phase. Furthermore, these results indicate that most of the extracted P is not directly related to Ca-carbonate associated P. The same release pattern of Ca and P can be discerned in the extraction of a sample consisting of pure calcite and a small addition of fish debris (Fig. 3B), indicating that the solubility of biogenic apatite is dependent on the Ca concentration in the solvent. Conversely, samples consisting of pure calcite and a small addition of detrital apatite and authigenic apatite show a lower solubility of the apatite in NH₄Cl respectively, and do not significantly respond to the drop in Ca concentration (Fig. 3C). The extracted P concentration remains low compared to the sample with fish debris. The similarity in the leaching patterns between sediment samples (Fig. 3A) and the calcite/fish debris sample (Fig. 3B) is consistent with the identification of the sedimentary P_{fish} fraction with biogenic apatite. Furthermore, these experiments show that at least eight NH₄Cl steps are required to ensure dissolution of the P_{fish} fraction in carbonate-rich sediments. The number of NH₄Cl steps could be diminished by reducing the solid-phase sample weight. However, this would lower the P concentration in the solvents, and accordingly, reduce the accuracy of the extraction method.

Additional evidence for the association of the P_{fish} fraction with biogenic apatite is obtained by comparing the extraction results with fish debris counts in the 150–595 μM fraction, assuming that the number of fish debris in this fraction is directly correlated to the fish debris content of the whole sample. Boxcore samples with high numbers of fish debris also have high P_{fish} concentrations (Fig. 4A). However, the correlation is not straightforward, as samples with low fish debris contents still contain substantial concentrations of P_{fish}. The latter samples all originate from boxcores taken in the deep Arabian basin. The larger water depth and lower sediment accumulation rates may have enhanced the fragmentation of fish particles. As a consequence, fish debris may have become under-represented in the 150–595 μm fraction. This is consistent with microscopical observations of the 65–150 μm fraction, where small fish debris particles seem more abundant.

Microscopical observations in the sieve fractions (150–595 μm, 65–150 μm) of pistoncore samples also indicate that samples with the highest P_{fish} concentrations have high contents of fish debris. Besides fish debris, these sieve fractions predominantly contain foraminifers. All foraminifers have a clean appearance indicating that they have no coatings of iron oxides or authigenic apatite. Chemical analysis of samples from which fish debris was removed by hand-picking, revealed that the P concentration of foraminiferal debris is indeed very low (<20 ppm), which is consistent with the results of Sherwood et al. (1987). Consequently, the P concentration of these fractions must be directly related to the fish debris content. The correlation between the P_{fish} concentration (whole sample) and the total P content in the 65–150 μm fraction is good for samples from both PC487 ($r^2 = 0.81$) and PC455 ($r^2 = 0.97$) (Fig. 4B). All these observations confirm the association of biogenic apatite with the P_{fish} fraction.

Other P fractions extracted in NH₄Cl are easily adsorbed P and porewater phosphate. Numerous studies (De Lange

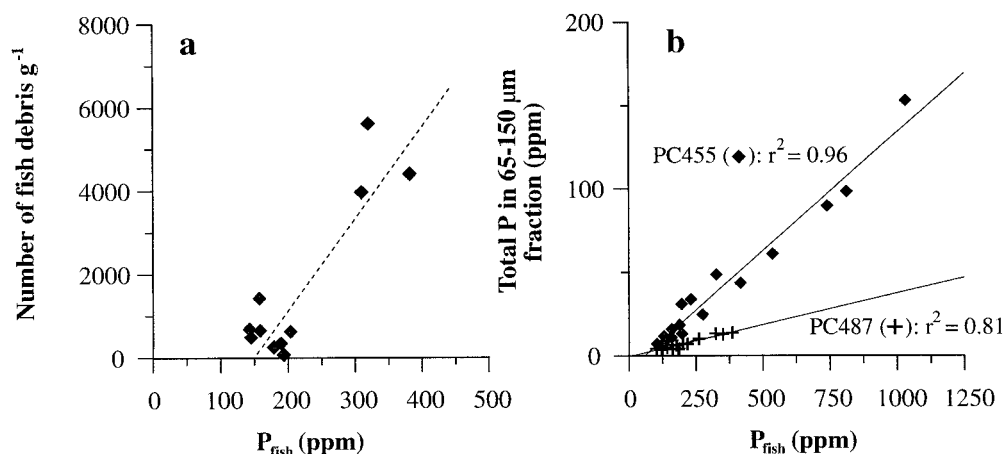


Fig. 4. A plot of a) P_{fish} concentrations versus number of fish debris in sediment surface samples (150–595 μm sieve fraction; see Table 1), and b) P_{fish} concentrations in total samples versus total P contents of the 65–150 μm sieve fraction in the same samples from PC455 and PC487. The difference in slope for samples from these cores is related to a different fish debris distribution over the sieve fractions.

1992; Ruttenberg and Berner 1993; Filippelli and Delaney 1996; Eijsink et al. 1997) have shown that the concentration of these fractions is usually low in marine sediments (<30 ppm), particularly compared to the total P concentration. During early diagenetic phosphogenesis, precipitation of carbonate fluorapatite (CFA) is often preceded by the formation of a F-poor precursor (Van Cappellen and Berner 1991; Krajewski et al. 1994). This precursor, which is precipitating in recent Arabian Sea sediments located within the oxygen minimum zone (OMZ), is also soluble in 2 M NH_4Cl (Schenau et al. submitted). Therefore, the NH_4Cl extraction cannot be used to differentiate between biogenic apatites and precursor apatite. However, in the sediment samples of this study, the contribution of such a precursor is insignificant (see below).

In conclusion, the NH_4Cl extraction is a good method to differentiate between CFA and more soluble biogenic apatites. Distinction between these two apatite phases has three advantages: (1) it enables the evaluation of the importance of fish debris burial in the marine phosphorus cycle, (2) it allows reconstruction of the deposition history of fish debris in sediment records, and (3) this method improves the determination of CFA burial rates. Furthermore, the results of this study indicate that the Ca-carbonate content of the sample is very important in determining the step in which biogenic apatite is extracted. For traditional extraction schemes (e.g., SEDEX method; Ruttenberg 1992), biogenic apatite may be extracted prematurely for sediment samples containing low carbonate contents (i.e., during the Na-dithionite extraction), and thus be attributed to the incorrect fraction. A direct extraction of “fresh” fish debris in the CDB solution (step 2, without the 2 M NH_4Cl rinse) indicated that biogenic apatite is also highly soluble in this extractant (dissolution of ca. 40 wt% fish debris of a 0.01 g sample in 25 ml CDB solution).

Distribution of fish debris in recent Arabian Sea sediments—The NH_4Cl extraction has been applied to samples

taken from surface sediments (upper 0–2 cm) of Arabian Sea boxcores. Because no (or very little) phosphogenesis takes place in the upper centimeter of these boxcores (Schenau et al. submitted), no interference of a possible precursor to CFA formation is expected for these samples. The P_{fish} concentrations are highest in sediments located at relatively shallow water depths (<1,200 m; Table 1). Because of dilution effects, the burial of fish debris is better represented by the deposition rates of P_{fish} , calculated as the product of the P_{fish} concentration and the mass accumulation rate. P_{fish} deposition rates decrease rapidly with increasing water depth (Fig. 5A). In sediments deeper than 1,200 m, P_{fish} deposition rates decrease more gradually with depth. Furthermore, high P_{fish} concentrations are associated with organic-rich sediments (Fig. 5B).

In the next sections we will discuss the two factors governing the accumulation of P_{fish} namely, (1) fish production, and (2) regeneration of fish debris in water column and sediment. The sub-recent (pre-fishery) fish production in the Arabian Sea is estimated in order to calculate the preservation potential of biogenic apatite in the underlying sediments.

(1) Fish production in the Arabian Sea: The Arabian Sea is one of the most productive areas in the world. Strong southwestern monsoonal winds cause coastal and open ocean upwelling off Somalia and Oman during the summer (e.g., Wyrski 1973; Slater and Kroopnick 1984). Due to upwelling nutrient-rich water masses are transported throughout the Arabian Sea, causing a high seasonal productivity (e.g., Qasim 1982). High downward fluxes of organic matter, in combination with restricted deep water ventilation, result in an extensive OMZ between 150 and 1,250 m depth (e.g., Slater and Kroopnick 1984). The high biomass of phyto- and zooplankton induces high rates of fish production in the Arabian Sea (Peterson 1991). The richest fishing areas are concentrated in the coastal waters of the Oman and Indian/Pakistan margins (Cushing 1973; FAO 1981; Venema 1984). How-

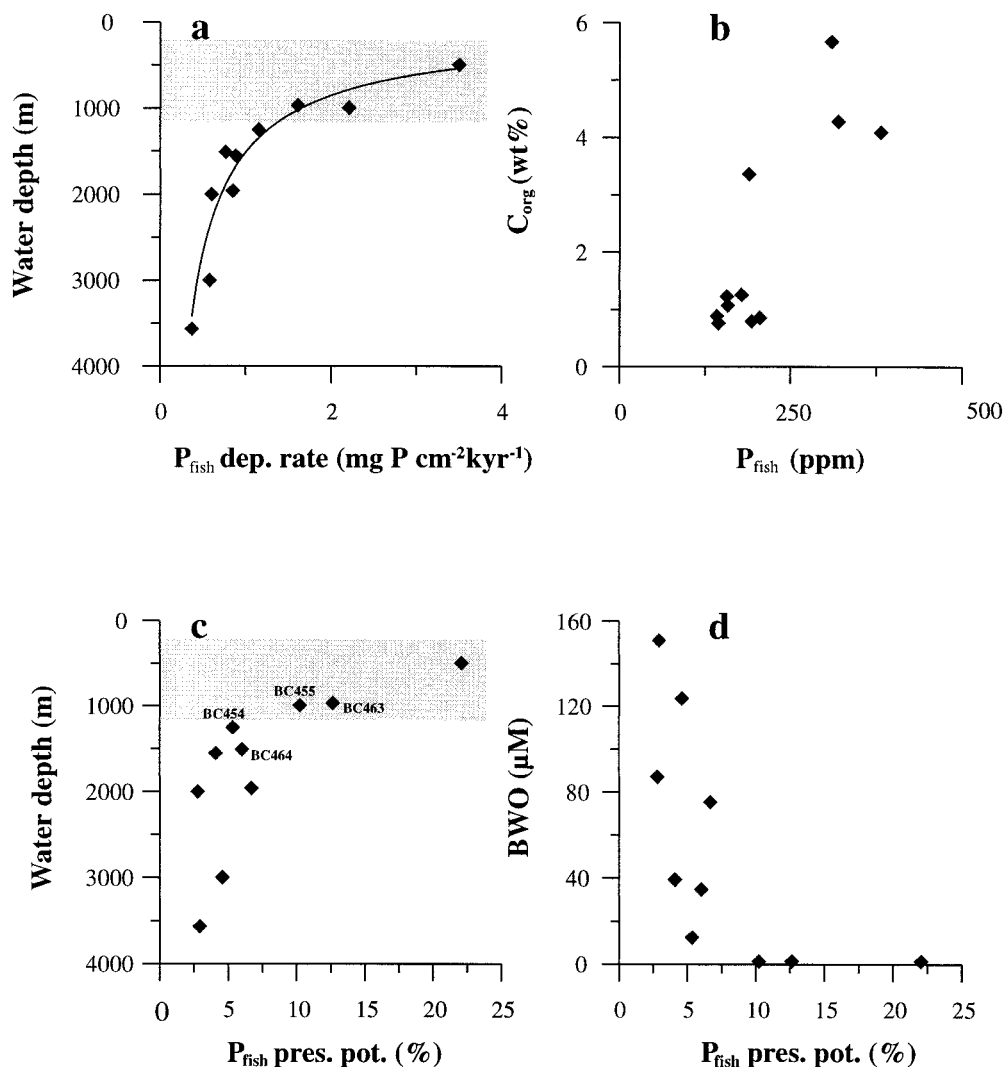


Fig. 5. A plot of (a) P_{fish} deposition rates ($\text{mg P cm}^{-2} \text{ k yr}^{-1}$) in sediment surface samples (see Table 1) versus water depth (m), (b) P_{fish} concentrations (ppm) versus organic carbon concentrations (wt%), and a plot of P_{fish} preservation potential (%) in sediment surface samples versus respectively (c) water depth (m), and (d) bottom water oxygen concentrations (μM). The solid line in a) represents a best fit $[P_{\text{fish}} \text{ deposition rate}] = 3745.9 \times [\text{water depth}]^{-1.124}$; ($r^2 = 0.93$). The shaded area indicates the position of the OMZ ($O_2 < 10 \mu\text{M}$).

ever, good estimates for total demersal and pelagic fish resources in this region are still lacking (FAO 1997).

The size of fish populations in the oceans is dependent on several factors, such as primary productivity, water temperature, water depth, and since recent times, the impact of increased fisheries (Sharp 1988). Food availability, however, is generally considered as the most important factor determining fish production in the oceans (e.g., Bailey and Robison 1986). Numerous efforts have been made to estimate fish production based on trophic dynamic models (e.g., Ryther 1969; Iverson 1990). However, uncertainty about the transfer efficiencies and food web structure makes good quantitative predictions for total fish production difficult (Haedrich and Merrett 1992). Estimating fish production rates from primary productivity data in the Arabian Sea is

even more complicated. First of all, the intensity of monsoon induced upwelling changes from year to year, and as a consequence, the annual primary productivity rate in this area is variable. For example, abundances of oil sardine offshore southwestern India, which are closely tied to the onset time and strength of coastal upwelling (Longhurst and Wooster 1990), have varied significantly over the last century. Secondly, the vertical distribution of fish populations in the water column is influenced by the presence of low-oxygenated waters at mid-water depth (Banse 1968; Röpke et al. 1993). Thirdly, dispersion processes may effect the distribution of fish populations over the surface waters, resulting in a distortion of the local food web (Sharp 1988).

Recognizing all these uncertainties, fish production (FP) ($\text{g m}^{-2} \text{ yr}^{-1}$, wet weight) in the Arabian Sea was estimated

by means of the trophic-dynamic model developed by Iverson (1990), using the equation:

$$FP = (0.083 \times ACP - 3.08) \times E^n \times c_1 \times c_2 \quad (1)$$

where ACP is the phytoplankton annual carbon production ($\text{g C m}^{-2} \text{ yr}^{-1}$), E the transfer efficiency of nitrogen (0.28), n the number of trophic levels (2.5), c_1 the fish biomass C:N ratio (3.6:1), and c_2 the product of the ratio of fish dry weight to C (2.4) and the ratio of fish wet to dry weight (3.3), which equals 7.9. This model is based on the assumption that fish production is controlled by the amount of new N annually incorporated into phytoplankton biomass, which is subsequently transferred into the food chain. An average number of 2.5 for the trophic levels (n) has been found to apply to many marine environments (Iverson 1990).

Estimates for present-day annual primary productivity in the northwestern Arabian Sea vary between 100 and 350 $\text{g C m}^{-2} \text{ yr}^{-1}$ (e.g., Qasim 1982; Olsen et al. 1993; Jochem et al. 1993). Mean annual productivity for the coastal region of the Pakistan Margin is likely to be somewhat higher than in the central basin due to a deepening of the mixed layer during the winter, which injects nutrients into the surface waters (Wyrski 1973). For this study, we have used the results of a photosynthesis-irradiance model (Brock et al. 1994), where the average daily rate of mixed-layer primary production in the Arabian Sea was estimated for each season, resulting in a mean primary productivity rate of 280 $\text{g C m}^{-2} \text{ yr}^{-1}$ for the Pakistan Margin and 180 $\text{g C m}^{-2} \text{ yr}^{-1}$ more offshore. Applying these values to the model of Iverson (1990), the calculated fish production for the Pakistan Margin and the northern Arabian Basin amount to 23.8 $\text{g m}^{-2} \text{ yr}^{-1}$ and 14.0 $\text{g m}^{-2} \text{ yr}^{-1}$ respectively. These fish production rates are high compared to other oceanic and coastal regions (Iverson 1990; Haedrich and Merrett 1992), which can probably be attributed to the eutrophic nature of the northern Arabian Sea.

(2) Regeneration of fish debris in the water column and sediment: The amount of fish debris that eventually is buried is affected by dissolution occurring in the water column and in the sediment. Processes governing the dissolution of fish debris in the marine environment are not well known. In the upwelling area offshore Peru approximately 10 wt% of P associated with fish bones produced in the surface waters is estimated to be preserved upon burial (Suess 1981; Froelich et al. 1982). Water depth, which determines the transit time through the water column, may be an important factor controlling preservation of fish debris. DeVries and Percy (1982) observed the highest concentrations of fish debris in sediments deposited at water depths <600 m, whereas less well-preserved material was found in deeper water. However, fish particles are relatively large and have a high density compared to seawater, which will make them sink relatively fast to the seafloor. Dissolution will, therefore, occur primarily after deposition, and not during transfer through the water column.

Dissolution of fish debris will continue after burial in the sediment (e.g., Nriagu 1983). High subsurface porewater phosphate concentrations observed in continental slope sediments often cannot be explained exclusively by phosphate

release from organic matter degradation or iron oxide reduction (Froelich et al. 1988; Van Cappellen and Berner 1988; Schuffert et al. 1994). Some of these high porewater phosphate concentrations, therefore, have been attributed to the dissolution of fish debris (Suess 1981; Van Cappellen and Berner 1988). A significant fraction of P associated with fish debris may thus be regenerated during early diagenesis. Decomposition of fish bone apatite in sediments is dependent on many factors, including porewater pH, phosphate and calcium porewater concentrations, destruction by microorganisms, winnowing, and bioturbation (Atlas and Pytkowicz 1977; Newsly 1989). Furthermore, higher mass accumulation rates promote incorporation into the sediment before complete dissolution occurs (Froelich et al. 1982). Potentially, redox conditions of bottom water and pore water may effect the preservation of biogenic apatite. Organic matter remineralization under oxygenated conditions produces acidity, which induces the dissolution of carbonates and, possibly, biogenic apatite in deep-sea sediments (e.g., Canfield and Raiswell 1991; Thomson et al. 1998). However, during suboxic (denitrification, Mn- and Fe-oxide reduction) and anoxic (sulphate reduction) diagenesis, no acidity is produced (provided that H_2S is consumed by pyrite formation; Canfield and Raiswell 1991), potentially leading to less dissolution of fish debris. Furthermore, phosphate concentrations of the interstitial water of anoxic sediments are usually high due to high rates of organic matter degradation. This will also decrease the dissolution rate of fish debris. Consequently, sediments located within a suboxic environment may experience enhanced preservation of biogenic apatite.

To assess the factors controlling the burial of fish debris in the Arabian Sea, preservation potentials (pres%) of P_{fish} for the boxcore samples were calculated using the following equation:

$$\text{pres\%} = 100 \times \frac{P_{\text{fish dep.}}}{FP \times [P]_{\text{fish}}/c_3} \quad (2)$$

where $P_{\text{fish dep.}}$ is the P_{fish} deposition rate ($\text{g P m}^{-2} \text{ yr}^{-1}$), FP the fish production rate ($\text{g m}^{-2} \text{ yr}^{-1}$; as calculated with Eq. 1), $[P]_{\text{fish}}$ the phosphorus dry weight fraction of marine fishes (0.03, Anonymous 1982), and c_3 the ratio of fish wet weight % to fish dry weight % (3.3; Iverson 1990). It should be noted that the preservation potential calculated with this equation incorporates only regeneration of P_{fish} during its transit through the water column and in the upper 2 cm of the sediment, and therefore, is not equal to the total burial efficiency. So the preservation potential, therefore, must be interpreted as a maximum value for the P_{fish} burial efficiency, because further dissolution may occur deeper in the sediment. The P_{fish} preservation potentials vary between 3 and 6% for the boxcores located deeper than 1,200 m (Fig. 5C). The three boxcores located at shallower water depths (BC451, BC455, and BC463) all have a significantly higher P_{fish} preservation potential (10–22%). The absolute values must be considered with some caution due to relatively large uncertainties for the calculated fish production rates and the value used for the dry weight P fraction of marine fishes. However, these results do demonstrate a distinct contrast in P_{fish} regeneration for different areas of the Arabian Sea.

Differences in P_{fish} deposition rates are much larger than variations in fish production, indicating that the distribution of fish debris in the surface sediments of the Arabian Sea is predominantly governed by regeneration processes. This is also illustrated by the relatively large differences in P_{fish} preservation potential between BC455 and BC454, and between BC463 and BC464 (Fig. 5C). The sample sites of these box-cores are located in close proximity to each other, and therefore, fish production in the water column must have been approximately the same. The higher preservation potentials in sediments of relatively shallow water depth can be attributed to shorter transit times through the water column, higher sedimentation rates, and lower BWO concentrations. It is not possible to determine the relative importance of each of these factors, but the close association between low BWO concentrations and high preservation potentials (Fig. 5D) suggests that more reducing bottom water conditions may have decreased dissolution of fish bone apatite. We therefore speculate that enhanced preservation of fish debris under oxygen depleted conditions may partly explain the high percentages of fish debris often observed in laminated sediments (Souter and Isaacs 1974; De Vries and Pearcy 1982; this study).

Conclusions

Phosphorus associated with biogenic apatite is highly soluble in 2 M NH_4Cl . Standardization experiments indicate that only small percentages of authigenic apatite, detrital apatite, and iron-bound P are extracted in NH_4Cl . Therefore, a sequential extraction with 2 M NH_4Cl (repeated 8 times), is a good method to separate P associated with fish debris (P_{fish}) from other sedimentary P fractions. Distinction between the biogenic and authigenic apatite phases has three advantages. Firstly, it enables evaluation of the importance of fish debris burial in the marine phosphorus cycle. Secondly, it allows reconstruction of the deposition history of fish debris in sediment records. Thirdly, application of this extraction scheme improves the determination of authigenic apatite burial rates.

The P_{fish} deposition rates in the surface sediments of the Arabian Sea are predominantly governed by differences in P_{fish} regeneration in sediment and water column. Preservation of fish debris is higher in sediments located at relatively shallow water depths (<1,200 m), which is related to shorter transit times through the water column, higher sediment accumulation rates, and lower bottom water oxygen concentrations.

References

- ANONYMOUS. 1982. Kirk—Othmer Encyclopedia of chemical technology, 3rd ed., V. 17. Wiley.
- ARRHENIUS, G. O. 1963. Pelagic sediments, p. 655–727. In M.N. Hill, [ed.], The sea. V. 3. Wiley.
- ATLAS, E., AND R. M. PYTKOWICZ. 1977. Solubility behaviour of apatites in seawater. *Limnol. Oceanogr.* **22**: 290–300.
- BANSE, K. 1968. Hydrography of the Arabian Sea Shelf of India and Pakistan and effects on demersal fishes. *Deep-Sea Res.* **15**: 45–79.
- BAILEY, T. G., AND B. H. ROBISON. 1986. Food availability as a selective factor on the chemical compositions of midwater fishes in the eastern North Pacific. *Mar. Biol.* **91**: 131–141.
- BERNER, R. A., K. C. RUTTENBERG, E. D. INGALL, AND J.-L. RAO. 1993. The nature of phosphorus burial in modern marine sediments, p. 365–378. In R. Wollast, F. T. Mackenzie, and L. Chou [eds.], Interactions of C, N, P, and S biogeochemical cycles and global change. NATO ASI Series. Vol. 14. Springer.
- BROCK, J., S. SATHYENDRANATH, AND T. PLATT. 1994. A model study of seasonal mixed layer primary production in the Arabian Sea, p. 65–78. In D. Lal [ed.], Biogeochemistry of the Arabian Sea. Ind. Acad. Sci.
- CANFIELD, D. E., AND R. RAISWELL. 1991. Carbonate precipitation and dissolution, its relevance to fossil preservation, p. 411–453. In P. A. Allison and D. E. G. Briggs [eds.], Taphonomy: Releasing the data locked in the fossil record, Topics in Geobiology. Vol. 9. Plenum.
- CUSHING, D. H. 1973. Production in the Indian Ocean and the transfer from the primary to the secondary level, p. 475–486. In B. Zeitschel [ed.], The biology of the Indian Ocean. Springer.
- DE LANGE, G. J. 1992. Distribution of various extracted phosphorus compounds in the interbedded turbiditic/pelagic sediments of the Madeira Abyssal Plain, eastern North Atlantic. *Mar. Geol.* **109**: 115–139.
- DEVRIES, T. J., AND W. G. PEARCY. 1982. Fish debris in sediments of the upwelling zone off central Peru: A late Quaternary record. *Deep-Sea Res.* **28**: 87–109.
- DIESTER-HAAS, L. 1978. Sediments as indicators of upwelling, p. 261–281. In R. Boje and M. Tomczak [eds.], Upwelling ecosystems. Springer.
- EIJSINK, L. M., M. D. KROM, AND G. J. DE LANGE. 1997. The use of sequential extraction techniques for sedimentary phosphorus in eastern Mediterranean sediments. *Mar. Geol.* **139**: 147–155.
- FAO. 1981. Atlas of the living resources of the Sea. FAO, Rome, 4th ed.
- . 1997. Review of the state of world fishery resources: Marine fisheries. 8. Western Indian Ocean. FOA Fisheries circular No. 920 FIRM/C920. FAO, Rome.
- FILIPPELLI, G. M., AND M. L. DELANEY. 1996. Phosphorus geochemistry of equatorial Pacific sediments. *Geochim. Cosmochim. Acta* **60**: 1479–1495.
- FROELICH, P. N., M. L. BENDER, N. A. LUEDTKE, G. R. HEATH, AND T. DEVRIES. 1982. The marine phosphorus cycle. *Am. J. Sci.* **282**: 474–511.
- , M. A. ARTHUR, W. C. BURNETT, M. DEAKIN, V. HENSLEY, R. JAHNKE, L. KAUL, K.-H. KIM, K. ROE, A. SOUTAR, AND C. VATHAKANON. 1988. Early diagenesis of organic matter in Peru continental margin sediments: Phosphorite precipitation. *Mar. Geol.* **80**: 309–343.
- HAEDRICH, R. L., AND N. R. MERRETT. 1992. Production/biomass ratios, size frequencies, and biomass spectra in deep-sea demersal fishes, p. 157–182. In G. T. Rowe and V. Pariente [eds.], Deep-sea food chains and the global carbon cycle. Kluwer.
- IVERSON, R. L. 1990. Control on marine fish production. *Limnol. Oceanogr.* **35**: 1593–1604.
- JOCHEM, F. J., F. POLLEHNE, AND B. ZEITZSCHEL. 1993. Productivity regime and phytoplankton size structure in the Arabian Sea. *Deep-Sea Res.* **40**: 711–735.
- KRAJEWSKI, K. P., P. VAN CAPPELLEN, J. TRICHET, O. KUHN, J. LUCAS, A. MARTÍN-ALGARRA, L. PRÉVÔT, V. C. TEWARI, L. GASPARD, R. I KNIGHT, AND M. LAMBOY. 1994. Biological processes and apatite formation in sedimentary environments. *Eclogae Geol. Helv.* **87**: 701–745.
- LONGHURST, A. R., AND W. S. WOOSTER. 1990. Abundance of oil sardine (*Sardinella longiceps*) and upwelling on the southwest coast of India. *Can. J. Fish. Aquat. Sci.* **47**: 2407–2419.
- LORD, C. J. III. 1982. A selective and precise method for pyrite

- determination in sedimentary materials. *J. Sed. Petr.* **52**: 664–666.
- LOWENSTAM, H. A. 1972. Phosphatic hard tissues of marine invertebrates: Their nature and mechanical function, and some fossil implications. *Chem. Geol.* **9**: 153–166.
- NEMLIHER, J., T. KALLASTE, AND I. PUURA. 1997. Hydroxyapatite varieties in recent fish scales. *Proc. Estonian Acad. Sci. Geol.* **46**: 187–196.
- NEWESLY, H. 1989. Fossil bone apatite. *Appl. Geochem.* **4**: 233–245.
- NRIAGU, J. O. 1983. Rapid decomposition of fish bones in Lake Erie sediments. *Hydrobiologia* **106**: 217–222.
- OLSEN, D. B., G. L. HITCHCOCK, R. A. FINE, AND B. A. WARREN. 1993. Maintenance of the low-oxygen layer in the central Arabian Sea. *Deep-Sea Res. II* **40**: 673–685.
- PETERSON, W. T. 1991. Zooplankton and nekton in the Arabian Sea, p. 75–85. *In* S. L. Smith et al. [eds.], U.S. JGOFS Planning report No. 13.
- POSNER, A. S., N. C. BLUMENTHAL, AND F. BETTS. 1984. Chemistry and structure of precipitated hydroxyapatites, p. 330–350. *In* J. O. Nriagu, and P. B. Moore [eds.], *Phosphate minerals*. Springer.
- QASIM, S. Z. 1982. Oceanography of the northern Arabian Sea. *Deep-Sea Res.* **29**: 1041–1068.
- RÖPKE, A., W. NELLEN, AND U. PIATKOWSKI. 1993. A comparative study on the influence of the pycnocline on the vertical distribution of fish larvae and cephalopod paralarvae in three ecologically different areas of the Arabian Sea. *Deep-Sea Res. II* **40**: 801–819.
- RUTTENBERG, K. C. 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnol. Oceanogr.* **37**: 1460–1482.
- , AND R. A. BERNER. 1993. Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. *Geochim. Cosmochim. Acta* **57**: 991–1007.
- RYTHER, J. H. 1969. Photosynthesis and fish production in the sea. *Science* **166**: 72–76.
- SCHENAU, S. J. 1999. Cycling of phosphorus and manganese in the Arabian Sea during the Late Quaternary. *Geologica Ultraiectina* 182, Ph.D. thesis. Utrecht University.
- SCHMITZ, B., G. ÅBERG, L. WERDELIN, P. FOREY, AND S. E. BENDIX-ALMGREEN. 1991. $^{87}\text{Sr}/^{86}\text{Sr}$, Na F, Sr and La in skeletal fish debris as a measure of the paleosalinity of fossil-fish habitats. *Geol. Soc. Am. Bull.* **103**: 786–794.
- SCHUFFERT, J. D., R. A. JAHNKE, M. KASTNER, J. LEATHER, A. STURZ, AND M. R. WING. 1994. Rates of formation of modern phosphorite off western Mexico. *Geochim. Cosmochim. Acta* **58**: 5001–5010.
- SHARP, G. D. 1988. Fish populations and fisheries, their perturbations, natural and man-induced, p.155–202. *In* H. Postma, and J. J. Zijlstra [eds.], *Continental shelves*. Elsevier.
- SHERWOOD, B. A., S. L. SAGER, AND H. D. HOLLAND. 1987. Phosphorus in foraminiferal sediments from North Atlantic Ridge cores and in pure limestones. *Geochim. Cosmochim. Acta* **51**: 1861–1866.
- SLATER, R. D., AND P. KROOPNICK. 1984. Controls on dissolved oxygen distribution and organic carbon deposition in the Arabian Sea, p. 305–312. *In* B. U. Haq, and J. D. Milliman [eds.], *Geology and oceanography of the Arabian Sea and Coastal Pakistan*.
- SOUTAR, A., AND J. D. ISAACS. 1974. Abundance of pelagic fish during the 19th and 20th centuries as recorded in anaerobic sediments off the Californias. *Fish Bull.* **72**: 257–274.
- SUESS, E. 1981. Phosphate regeneration from sediments of the Peru continental margin by dissolution of fish debris. *Geochim. Cosmochim. Acta* **45**: 577–588.
- THOMSON, J., I. JARVIS, D. R. H. GREEN, D. A. GREEN, AND T. CLAYTON. 1998. Mobility and immobility of redox-sensitive elements in deep-sea turbidites during shallow burial. *Geochim. Cosmochim. Acta* **62**: 643–656.
- TRAPPE, J. 1998. Phanerozoic phosphorite depositional systems. A dynamic model for a sedimentary resource system. *Lecture notes in earth science* 76. Springer.
- VAN CAPPELLEN, P., AND R. A. BERNER. 1988. A mathematical model for the early diagenesis of phosphorus and fluorine in marine sediments: Apatite precipitation. *Am. J. Sci.* **288**: 289–333.
- , AND ———. 1991. Fluorapatite crystal growth from modified seawater solutions. *Geochim. Cosmochim. Acta* **55**: 1219–1234.
- VAN DER WEIDEN, C. H., G. J. REICHAERT, AND H. J. VISSER. 1999. Enhanced preservation of organic matter in sediments deposited within the oxygen minimum zone in the northeastern Arabian Sea. *Deep-Sea Res.* **46**: 807–830.
- VENEMA, S. C., 1984. Fishery resources in the north Arabian Sea and adjacent waters. *Deep-Sea Res.* **31**: 1001–1018.
- WYRTKI, K. 1973. Physical oceanography of the Indian Ocean, p. 18–36. *In* B. Zeitschel [ed.], *The biology of the Indian Ocean*. Springer.

Received: 11 May 1999

Accepted: 13 December 1999

Amended: 19 January 2000