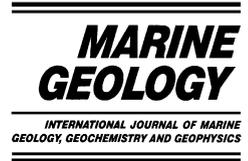




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Authigenic P formation and reactive P burial in sediments of the Nazaré canyon on the Iberian margin (NE Atlantic)

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Abstract

Profiles of different forms of sedimentary phosphorus were measured at four sites at the Iberian margin (NE Atlantic), which were chosen on the basis of differences in depositional environment: a shelf site (113 m), a mid-slope station (1387 m) and two stations at the head (396 m) and base (3097 m) of the Nazaré Canyon. The sediment was sequentially extracted for Fe-bound P, carbonate fluorapatite (CFA)+biogenic P+CaCO₃-bound P and detrital Ca-P, and non-sequentially for total P and inorganic P, where the difference between total and inorganic P was assumed to be organic P. Measurements of organic carbon and nitrogen, citrate–dithionite–bicarbonate- and citrate–ascorbate–bicarbonate-extractable Fe, carbon oxidation rates, Fe reduction rates, phosphate effluxes and sedimentation rates were used to quantify the cycling and burial of phosphorus at each site. CFA formation was observed only in sediments of the Nazaré canyon, where enhanced rates of organic matter decomposition and Fe reduction provided the necessary conditions. The concentrations of reactive P were similar at all sites, but the sediment accumulation rates differed greatly. The high bulk accumulation rate at the base of the canyon results in a reactive P burial rate exceeding those estimated for continental margins including the Iberian margin by an order of magnitude. The estimated P burial efficiency is smallest at the slope station (3–24%), reasonably high (63–86%) at the shelf and head of the canyon stations and extremely high (>97%) at the base of the canyon. We propose that local depositories such as those at the base of canyons may be key sites for reactive P burial. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: phosphorus; diagenesis; geochemistry; NE Atlantic; Nazaré Canyon; Iberian continental margin

1. Introduction

Recycling and removal of phosphorus in the marine environment are important controls on

marine productivity, over both geological and shorter time scales (Holland, 1978; Broecker, 1982; Howarth et al., 1995; Van Cappellen and Ingall, 1996). Most removal of P from the water column takes place through sedimentation of organic material on continental margins (Berner, 1982; Froelich et al., 1982). Phosphorus is most effectively sequestered in sediments with oxygenated overlying bottom waters, via the formation of refractory organic P compounds (Ingall et al.,

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1990) and through binding to Fe oxides (Krom and Berner, 1981; Slomp et al., 1996b; Ingall and Jahnke, 1997). Phosphate is released into the pore water both upon organic matter degradation and upon reduction of Fe oxides loaded with P. In the reduced part of the sediment, phosphate release can lead to supersaturation of the pore waters with respect to authigenic P minerals and, consequently, carbonate fluorapatite (CFA) precipitates (Ingall and Van Cappellen, 1990; Ruttenger and Berner, 1993; Ingall and Jahnke, 1997). The formation of CFA may occur at the expense of either organic P or Fe-bound P (Ruttenger and Berner, 1993; Lucotte et al., 1994). Slomp et al. (1996a) proposed a mechanism for early diagenetic CFA formation in which Fe-bound P acts as an intermediate between organic P and CFA at the Goban Spur continental margin (NE Atlantic).

Recently, Filippelli (1997) showed that ranges of sedimentary P concentrations are comparable between continental margins and the deep sea environment. However, P accumulation rates are higher on the margin due to much higher sedimentation rates (Ruttenger, 1993). Very high P concentrations are found in areas on the continental margin, where significant phosphogenesis takes place, but these phosphorite deposits do not represent significant sinks in the marine P cycle due to very low sedimentation rates (Filippelli, 1997). Authigenic CFA, a major sedimentary P sink, is not restricted to active coastal upwelling areas, thus 'normal' continental margin sediments are a significant sink for reactive P in the ocean (Ruttenger, 1993; Filippelli, 1997). Continental shelves and slopes can function as traps for both terrestrial and marine particulate material, whereas submarine canyons incising the continental margin can act as preferential conduits for particulate material from the shelf to the deep sea (Carson et al., 1986; Gardner, 1989; Granata et al., 1999). The hydrodynamic conditions, size and morphology of the canyon and its location relative to continental sources have great impact on its potential for organic matter accumulation (Buscail and Germain, 1997; Etcheber et al., 1999). Sedimentation rates found in some canyons, particularly near the mouth, are much

higher than those found on open slopes (Carpenter et al., 1982; Cremer et al., 1999). Thus, P burial is potentially important in sediments of the shelf and slope as well as in high deposition areas of canyons and their fans.

The present study on P cycling was carried out within the framework of the Ocean Margin EXchange project (OMEX-II) at the Iberian continental margin. Other studies on elemental cycling at the Iberian margin have focused on carbon and nitrogen (Epping et al., 2002), manganese (Van der Zee et al., 2001), iron (Van der Zee et al., submitted) and silica (Koning et al., in preparation). The Iberian shelf is relatively narrow and interspersed with numerous canyons, amongst which is a large submarine canyon in the south of the margin, the Nazaré Canyon. This canyon represents an active locus for sediment focusing and deposition on the Iberian Margin (Schmidt et al., 2001; Van Weering et al., 2002). Enhanced organic matter deposition fluxes like those found in the Nazaré Canyon (Epping et al., 2002) also imply an enhanced P flux to the sediment since organic matter is the most important carrier of P to the sediment (Froelich et al., 1982; Berner et al., 1993). In this study, P cycling and burial are investigated in sediments of (1) a depositional area on the shelf, (2) a slope site, (3) a sandy area at the head of the Nazaré Canyon and, (4) a depositional area at the base of the Canyon. The objectives were (1) to make a comparison between P cycling at the depositional shelf and canyon stations and the sandy shelf and slope site and (2) to study the potential of the canyon as sink for reactive P. A modified version of the SEDEX scheme (Ruttenger, 1992) was applied to our sediments. First, we address the organic matter deposited at these contrasting sites using C/N and C/P ratios. Second, the inorganic P geochemistry is discussed, i.e. P interactions with Fe cycling and apatite precipitation. Finally, we conclude with a discussion on phosphorus burial in these different continental margin environments.

2. Study area

Our research area comprises the Iberian Margin

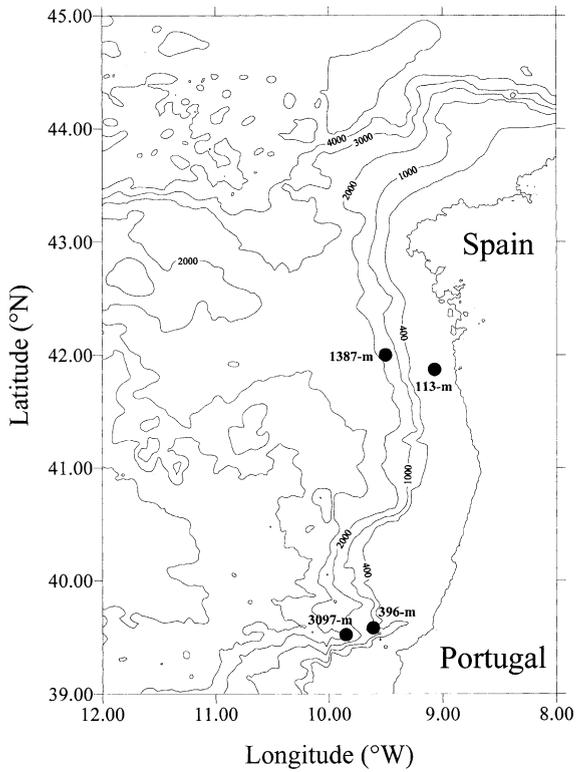


Fig. 1. Map of the Iberian Margin indicating the positions of the stations and the water depth.

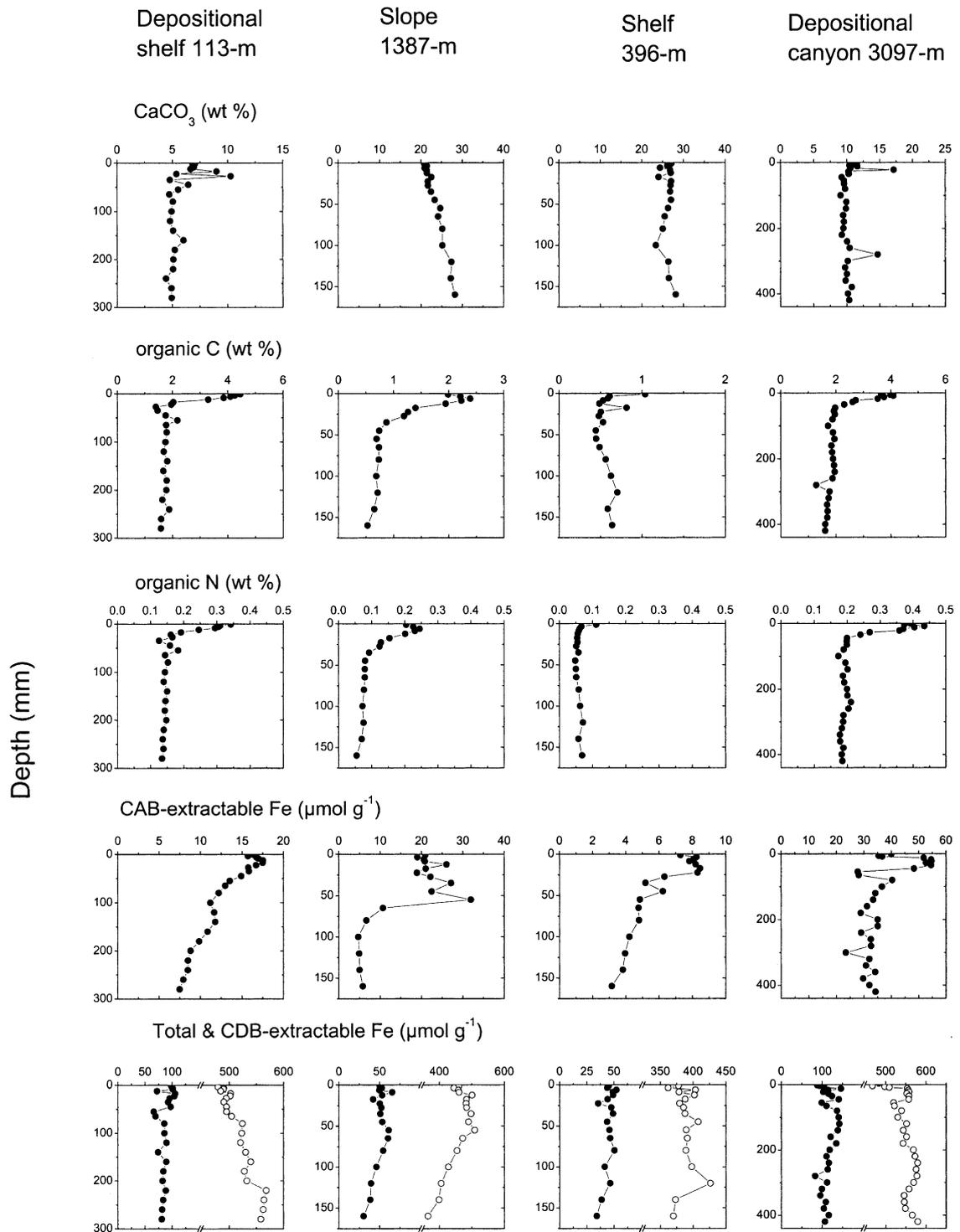
in the NE Atlantic (Fig. 1). The Iberian shelf is relatively narrow (200-m isobath situated at 15–30 km offshore). Seasonal upwelling invokes temporal high primary productivity and benthic carbon deposition. However, the carbon oxidation rates are relatively low compared to other upwelling areas, e.g. the Chilean margin (Epping et al., 2002). Sediment transport and accumulation in this region are described by Van Weering et al. (2002). Organic carbon oxidation rates in the sediment decrease with water depth, from ~ 11 on the shelf to $\sim 2 \text{ g C m}^{-2} \text{ yr}^{-1}$ at 5 km depth on the open slope (i.e. non-canyon sites). In the Nazaré canyon sediment is focussed, leading to sedimentation rates exceeding those of the adjacent shelf (Van Weering et al., 2002). The Nazaré canyon is quantitatively important in concentrating organic matter, resulting in carbon oxidation rates three times higher at the 3097-m canyon base compared

to sites at similar water depth outside of the canyon (Epping et al., 2002). Four of the Iberian Margin stations that were sampled during the PE138 cruise with RV *Pelagia* in May 1999 were selected for this study. The two northern stations are (1) a 113-m station located in a depositional area on the shelf and (2) a mid-slope station at 1387-m water depth. The two southern stations are (1) a 396-m station located near the head of the Nazaré canyon and (2) a 3097-m station situated in the depositional area at the base of the Nazaré canyon.

3. Materials and methods

Sediment cores were taken with a multi-corer equipped with polycarbonate liners and processed at in situ temperature directly upon retrieval. Four sediment cores were sliced simultaneously with a hydraulic core slicer developed at NIOZ. The sediment was sectioned in 2.5-mm slices in the upper centimeter of the sediment, 5-mm slices from 10 to 30 mm, 10-mm slices from 30 to 60 mm and 20-mm slices further down core. Slices from corresponding depth intervals were pooled and centrifuged ($5000 \times g$, 10 min) for separation of the interstitial water from the solid phase. The centrifuged sediment was stored frozen (-20°C) until further analysis for solid-phase constituents at the NIOZ laboratory.

Freeze-dried and ground sediment (Teflon or agate mortar and pestle) was extracted for solid-phase P according to Ruttenberg (1992) as modified by Slomp et al. (1996a). The sediment is sequentially extracted for Fe-bound P, CFA+biogenic P+CaCO₃-bound P, and detrital Ca-P. Fe-bound P was extracted as citrate–dithionite–bicarbonate-extractable P (CDB, pH 7.3, 8 h, 20°C) and the sediment residue was washed once with 1 M MgCl₂ (pH 8, 30 min, 20°C). CFA, biogenic P and CaCO₃-bound P were subsequently extracted with 1 M Na-acetate buffer (pH 4, 6 h, 20°C) and the sediment was washed again with 1 M MgCl₂ (pH 8, 30 min, 20°C). The rinses with MgCl₂ are necessary to reverse secondary adsorption. Finally the sediment residue was extracted with 1 M HCl (24 h, 20°C), which dis-



solves the detrital Ca-P. Organic P was determined as the difference between total P (total destruction, see below) and inorganic P (1 M HCl, 24 h, 20°C). Differences between the sum of the inorganic phases in the sequential procedure and the inorganic P extracted with 1 M HCl are due to propagation of the analytical errors. Therefore, we used the inorganic P values obtained by the single extraction instead of adding three values each with their own associated error. Analytical precision for the P extractions was better than 16% for Fe-bound P, 6% for authigenic P, 10% for detrital P, 3% for inorganic P and 2% for total P. Aliquots of the freeze-dried and ground sediment were additionally extracted with citrate–ascorbate–bicarbonate (CAB) solution for poorly crystalline Fe according to the method of Kostka and Luther (1994).

The P and Fe concentrations in the CDB extraction were determined using ICP-OES (Spectro Analytical Instruments). CDB-extractable Fe is assumed to consist of Fe from Fe oxides, although it may also extract some Fe from clay minerals and Fe sulfides (Slomp et al., 1996b). All other P analyses were performed on a Hitachi U-1100 spectrophotometer using the method of Strickland and Parsons (1972). Total P and Fe were determined after total destruction of the sediment with a mixture of HF, HNO₃ and HClO₄ and final solution of the residue in 1 M HCl using ICP-OES (Perkin Elmer Optima 3000). The Fe concentrations in the CAB extracts were measured on a Hitachi U-1100 spectrophotometer using the method of Stookey (1970). Total carbon and nitrogen and organic carbon were measured on a Carlo-Erba 1500 elemental analyzer (Verardo et al., 1990). CaCO₃ was determined as the difference between total and organic carbon. Total nitrogen is assumed to represent organic nitrogen (Lohse et al., 2000).

4. Results

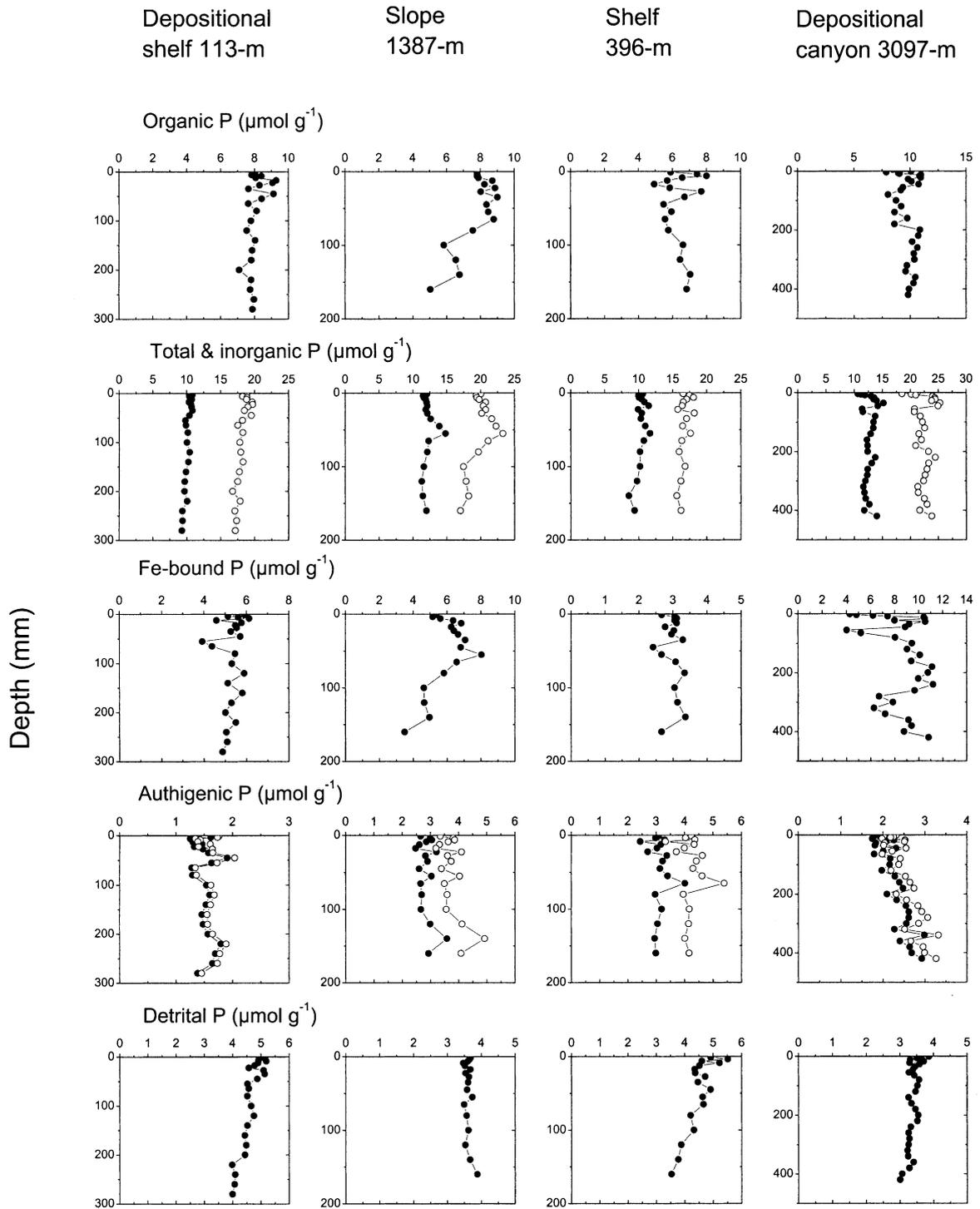
4.1. General sediment characteristics

The organic carbon contents are high (~4 wt%) in the 0–1-cm interval at the 113-m shelf and 3097-m canyon base depositional stations, whereas the CaCO₃ contents are low (~5–10 wt%) (Fig. 2). The CaCO₃ content is relatively high, ~20–30 wt%, at the 1387-m mid-slope station and at the 396-m site at the head of the canyon, whereas their organic carbon contents are lower, ~2 wt% and ~0.6 wt% in the 0–1-cm interval, respectively. CAB-extractable Fe profiles show clear (sub-)surface enrichments of Fe oxides formed upon re-oxidation of mobilized Fe²⁺ diffusing upward into the oxic layer. The concentration of CAB-extractable Fe is always lower than that extracted with CDB, suggesting a considerable contribution of relatively crystalline Fe oxides in the sediment. CDB-extractable Fe is a small percentage of the total Fe because the major fraction of Fe is bound in clay minerals (Raiswell and Canfield, 1998). Only at the 1387-m station is an enrichment in CDB-extractable Fe observed at the Fe redox boundary. The total and CDB-Fe contents are lower at the 396-m and 1387-m stations than at the depositional sites (113 m and 3097 m).

4.2. Solid-phase P profiles

Organic P varies only slightly with depth in the sediment at all locations, except at the 1387-m station where it decreases below ~65 mm depth (Fig. 3). Inorganic and total P decrease somewhat with depth at the 113-m and 396-m shelf stations. Subsurface maxima of inorganic and total P are observed at the 1387-m and 3097-m stations and the Fe-bound P profiles show the same trend. At

Fig. 2. Vertical profiles of calcium carbonate, organic carbon and nitrogen, CAB-extractable Fe, total (solid circles) and CDB-extractable (open circles) Fe. Organic carbon and nitrogen contents are high at the 113-m and 3097-m stations. Carbonate contents are relatively high at the 396-m and 1387-m stations. Fe enrichments at the redox boundary are most pronounced in the CAB-extractable fraction.



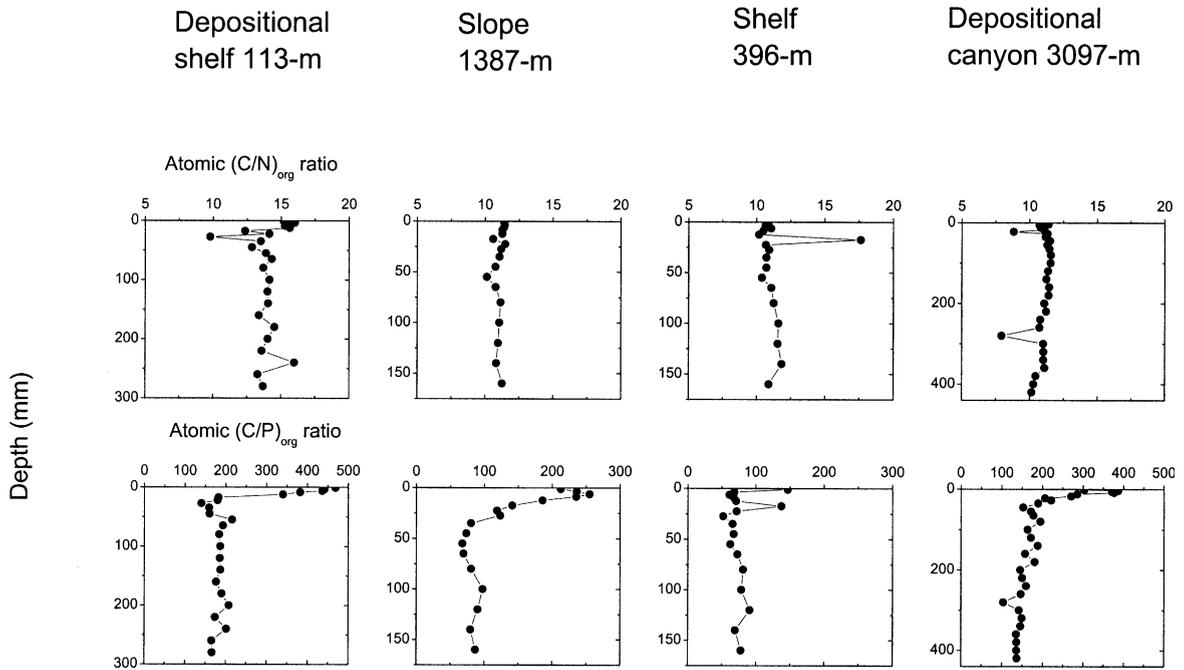


Fig. 4. Vertical profiles of organic carbon to nitrogen atomic ratios, and organic carbon to organic phosphorus atomic ratios. The atomic $(C/N)_{org}$ ratios are constant with depth (1387-m and 396-m sites) or decrease slightly (113-m and 3097-m sites), whereas the atomic $(C/P)_{org}$ ratios strongly decrease with depth, except at the 396-m site.

the shelf stations, Fe-bound P is relatively depth-invariant. Authigenic P profiles show some variation with depth at the shelf and slope stations. At the 3097-m station, it could be presently forming as indicated by the increase with depth. The lack of an increase in authigenic P with depth at the other stations does not necessarily preclude ongoing precipitation, since this could occur at the sediment–water interface or be masked by bioturbation. Both are probably not important at these stations because the pore water phosphate concentrations and gradients are rather low (E. Epping, personal communication) and do not indicate supersaturation of the pore waters with respect to authigenic P minerals and consequent CFA precipitation. The authigenic P profiles are also presented on a carbonate-free basis to assess

whether changes in the $CaCO_3$ flux can explain trends in the authigenic P profile, which is not the case. Detrital P is constant with depth at the 1387-m station, whereas it declines at the other three stations.

5. Discussion

5.1. Organic material

Organic C/N and C/P atomic ratios are used to characterize the organic material in the sediment (Fig. 4). The C_{org}/N ratios are constant with depth at the two organic-poor stations (396 m and 1387 m), whereas they slightly decrease with depth at the organic-rich stations (113 m and

Fig. 3. Vertical profiles of organic P, total (open circles) and inorganic (solid circles) P, iron-bound P, authigenic P (open circles are concentrations on a carbonate-free basis), and detrital P. Organic P was calculated as the difference between total P and inorganic P (1 M HCl-extractable P). Organic P declines strongly with depth, at the 1387-m slope station only. The authigenic P fraction is the sum of CFA, biogenic P and $CaCO_3$ -bound P. Authigenic P increases with depth at the 3097-m canyon station, whereas it does not show a distinct trend with depth at the other stations.

3097 m). At the 113-m station, the C_{org} content drops in the first 3 cm from 4.5 to 1.5 wt% and because the N content does not decrease similarly, the C_{org}/N ratio declines as well. The C_{org}/N signature of the sediment is probably caused by the terrestrial component in the organic matter at this depositional shelf station. Microscopic observations have revealed that remains of vascular plants are present in the sediment of the 113-m station. The C_{org}/N ratios of the other stations (1387, 396 and 3097 m) suggest an oceanic source of organic material.

The organic C/P profiles reflect the C_{org} trend with depth due to small variations in P_{org} with depth compared to C_{org} . Fresh marine planktonic organic matter has an average C/P ratio of about 106 (Redfield et al., 1963). The 113-m, 1387-m and 3097-m stations have higher organic C/P ratios at the sediment–water interface and decreasing values at depth suggesting that the organic matter arriving at the sediment–water interface is not fresh marine detritus. The microscopic observations and the C_{org}/N profile of the 113-m station indicated the presence of vascular plant material. As terrestrial plants can have C/P ratios as high as 800 (Simpson, 1977) to 2050 (Likens et al., 1981), this explains the high C/P ratio at the sediment–water interface of the 113-m station. The higher C/P ratios at the sediment–water interface of the 1387-m and 3097-m stations can be explained by preferential P regeneration under oxic decomposition in the water column during the ~ 200 and ~ 300 days prior to deposition at these stations, respectively (Epping et al., 2002). The lack of a decrease in organic P content with depth does not preclude changes in the nature of the organic P compounds with depth. The decreasing organic C/P ratio with depth in the sediment at the 1387-m and 3097-m stations can be caused by the formation of refractory material enriched in P, such as aminophosphonic acids (Ingall and Van Cappellen, 1990; Kittredge and Roberts, 1969). In situ synthesized bacterial biomass with a low C/P ratio might contribute to the decrease in the oxic layer of the sediment as well (Vadstein et al., 1988). At the 396-m station, the low organic C/P ratio is rather constant with depth, which may indicate that P is not preferen-

tially degraded or enriched in refractory material in the sediment. Thus, the decrease in C/P ratio with depth in the sediment can be explained by the presence of relatively labile organic matter deprived of P in the upper part of the sediment caused by preferential P degradation in the water column. Upon the degradation of organic matter, the relatively labile organic carbon is respired and the little P that is liberated is immediately re-incorporated in organic compounds. This has also been reported to occur during the oxidation of organic matter in sapropels (Slomp et al., 2002). The system is probably P-limited as suggested by the high C/P ratios supporting the re-incorporation hypothesis. As a consequence, organic P is efficiently retained in the sediment column.

Ingall and Van Cappellen (1990) argued that the sedimentation rate is the master variable of the burial ratio of organic carbon over organic phosphorus (C/P_{∞}) in a non-linear fashion. Low residual organic C/P_{∞} ratios (< 200) are typical for areas with sedimentation rates either < 0.002 cm yr^{-1} or > 1 cm yr^{-1} , whereas higher ratios, up to 600, are found in areas with intermediate sedimentation rates. Our shallowest stations have intermediate sedimentation rates (0.06 and 0.09 cm yr^{-1}), but nevertheless low residual C/P_{∞} ratios. This suggests that the organic P is of a relatively more refractory nature than organic C. The organic C/P_{∞} ratios of the canyon (1.45 cm yr^{-1}) and slope station (~ 0.001 – 0.01 cm yr^{-1}) are consistent with the model of Ingall and Van Cappellen (1990). The 396-m and 1387-m stations have lower C/P_{∞} ratios (75–90) and the 113-m and 3097-m stations have relatively higher C/P_{∞} ratios (140–160). All stations fall within the range of low residual C/P ratios. Thus, the P_{org} content that is buried is relatively high compared to the C_{org} content.

5.2. Inorganic P geochemistry

Fe oxides have a high affinity for phosphate (Berner, 1973; Slomp et al., 1996b) and consequently, Fe oxides present in the oxic layer of the sediment can act as a trap for upward diffusing phosphate (Krom and Berner, 1980; Sundby et al., 1992; Slomp et al., 1996a). When Fe oxides

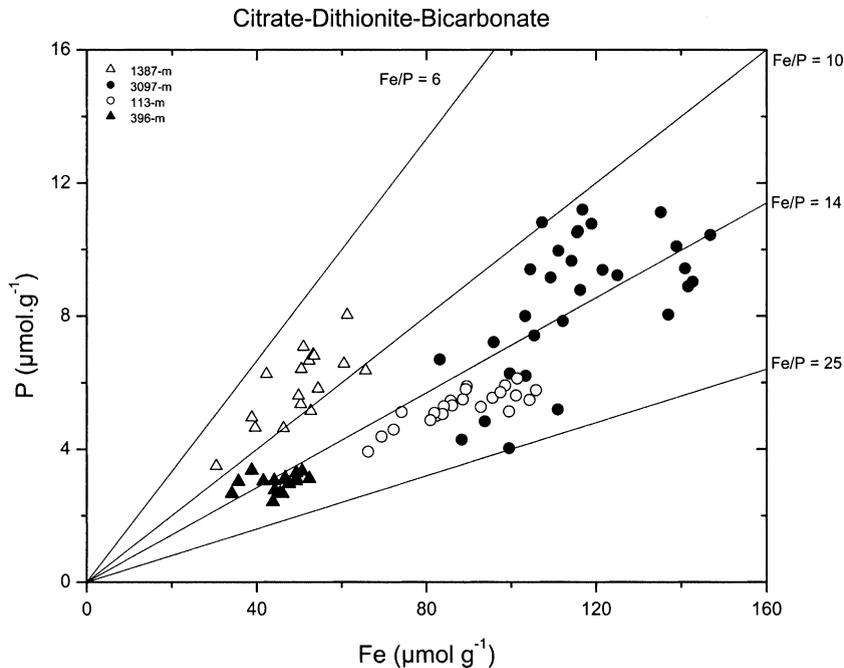


Fig. 5. CDB-extractable phosphorus versus iron in sediments of the 113-m (open circles), 1387-m (open triangles), 396-m (solid triangle) and 3097-m (solid circles) stations. The higher Fe/P ratios suggest that the CDB-extractable Fe oxides have a higher proportion of crystalline phases in those samples, which bind less phosphate per atom of Fe.

are reduced in the anoxic sediment layer the adsorbed phosphate is liberated, in addition to the P released during organic matter degradation (Krom and Berner, 1981). The Fe-bound P profiles do not show evidence of phosphorus enrichment due to Fe re-oxidation, except at the slope station. The Fe/P ratios for Iberian margin sediments extracted with a CDB range between 6 and 25 (Fig. 5). Jensen and Thamdrup (1993) reported Fe/P ratios of 6–8 for Aarhus Bay sediments, 10–16 for Kattegat sediments and a ratio of 17 for a station in the Skagerrak. An Fe/P ratio of 14 has been reported for suspended particles in the St. Lawrence estuary (Lucotte and d'Anglejan, 1988). Higher Fe/P ratios of 20–26 are reported for the North Atlantic and the Labrador Sea (De Lange, 1986; Lucotte et al., 1994). The high Fe/P ratio may indicate that the Fe oxides extracted with CDB have a higher proportion of relatively crystalline phases in those samples, because crystalline Fe phases bind less P while poorly crystalline Fe oxides have a higher P sorption capacity due to their larger surface areas (Borggaard,

1983). Poorly crystalline akageneite and ferrihydrite, identified by differential X-ray diffraction, proved to be the Fe phases that play a dominant role in P binding in North Sea sediments (Slomp et al., 1996b). Ascorbate is a milder reductant than dithionite and only extracts poorly crystalline Fe oxides (Kostka and Luther, 1994) that have a lower P sorption capacity. The CAB-extractable Fe concentration is only ~10–50% of the CDB-extractable Fe at our stations, which also indicates that a considerable amount of Fe in the sediment is of a more crystalline nature. Anschutz et al. (1998) extracted similar amounts of P, but not of Fe, with CDB and CAB from marine sediments, suggesting that P was only associated with poorly crystalline Fe. The Fe/P ratio was smaller and less variable using the CAB-Fe and P instead of the CDB-Fe and P (Anschutz et al., 1998). Fe-bound P has been suggested to represent a permanent sink of reactive P on continental margins (Ruttenberg and Berner, 1993; Jensen and Thamdrup, 1993; Slomp et al., 1996b). CDB-extractable Fe and Fe-bound P persist in the an-

Table 1

Names of stations, geographical location, water depth, bottom water oxygen concentration, bottom water temperature (BWT), median grain size (MGS) of the upper 2.5 mm (Van Weering et al., 2002), carbon oxidation rate (Epping et al., 2002) and Fe reduction rate (Van der Zee et al., submitted) of the sampled stations

Name	Lat.	Long.	Depth (m)	BW O ₂ (μM)	BWT (°C)	MGS (μm)	C ox rate (mmol m ⁻² day ⁻¹)	Fe red. (mmol m ⁻² day ⁻¹)
PE138-06	41.52	09.04	113	210	12.5	37.8	2.02	0.36
PE138-07	42.00	09.28	1387	188	10.3	15.1	1.02	0.04
PE138-15	39.35	09.37	396	200	11.6	69.4	1.42	0.09
PE138-14	39.31	09.51	3097	243	2.4	22.7	1.77	0.43

PE138-06 is at the shelf, PE138-07 at mid-slope, PE138-15 is at the head of the Nazaré Canyon and PE138-14 is at the base of the canyon.

oxic layer of the sediment, suggesting that Fe-bound P is at least a temporary sink on the Iberian margin.

The authigenic P fraction is the sum of CFA, biogenic P, such as fish debris, and CaCO₃-bound P. When expressed on a carbonate-free basis the trend with depth remains unchanged, indicating that changes in the CaCO₃ flux cannot explain the apparent increase of authigenic P with depth. It is possible that a larger contribution of biogenic P causes this increase, but there is no reason to assume that more fish debris is present deeper in the sediment as it is more prone to dissolution than authigenic apatite (Schenau et al., 2000). Although we cannot exclude the possibility that non-steady-state conditions are causing the authigenic P fraction to increase with depth, there is no indication for non-steady state from other solid-phase data, including organic carbon (Epping et al., 2002), manganese (Van der Zee et al., 2001) and natural radionuclides (Schmidt et al., 2001). We conclude that, most likely, CFA is forming in the sediment of the 3097-m station at the base of the canyon. The other solid-phase P fractions do not show a mirror image of the authigenic P, making a single particular source of P unlikely. The authigenic P formation could be fuelled by a combination of sources and because the increase is only moderate over the sampled interval, no clear decreases in the other P fractions are observed. CFA formation in marine sediments is important because it is a permanent sink of reactive P, whereas organic P and Fe-bound P can still be released after burial. The two prerequisites for authigenic P formation are high enough con-

centrations of phosphate for precipitation and nucleation sites (Van Cappellen and Berner, 1988). The required intense subsurface production of phosphate may not be produced solely by the decomposition of organic matter, but additional sources may be needed, e.g. dissolution of inorganic fish hard parts (Van Cappellen and Berner, 1988; Schenau et al., 2000) or release from Fe oxides (Slomp et al., 1996a). Phosphate release due to the reductive dissolution of Fe oxides is potentially most important at stations with higher Fe reduction rates, e.g. at the 113-m and 3097-m stations (Table 1). Incidentally, these stations also have the highest C oxidation rates. At the 3097-m station, both ammonia and dissolved Fe reach high concentrations (up to ~1100 μM and 360 μM, respectively) and are produced relatively deep in the sediment (Epping et al., 2002; Van der Zee et al., submitted). Thus, both organic matter degradation and Fe reduction rates are high and take place relatively deep in the sediment thereby providing the necessary conditions for the build-up of phosphate concentrations which are sufficiently high for authigenic P formation.

5.3. *Phosphorus burial*

The relative contributions of the P fractions to the pool of total P in our sediments (Table 2) differ greatly with those of deep-sea sediments of the equatorial Pacific investigated by Filippelli and Delaney (1996). They reported on P cycling at seven equatorial Pacific sites (2520–3861 m water depth), where authigenic P is the dominant P-bearing component (61–86%), followed by Fe-

Table 2

Bulk sediment accumulation rate (SAR) (Van Weering et al., 2002), total P content, total P burial rate, percentage of Fe-bound P, authigenic P, organic P and detrital P to total P

Water depth (m)	Bulk SAR ($\text{g m}^{-2} \text{ yr}^{-1}$)	Total P ($\mu\text{mol g}^{-1}$)	P burial ($\text{mmol m}^{-2} \text{ yr}^{-1}$)	Fe-bound P (%)	Auth. P (%)	Org. P (%)	Detrital P (%)
113	809	17.2	13.9	29	9	46	23
1387	~10–100	17.1	~0.2–1.7	24	19	33	21
396	634	16.2	10.3	19	19	44	23
3097	9623	22.3	215	39	11	44	15

P concentrations of the two deepest sampled intervals are averaged, except for the 3097-m station, where it is an averaged value over the 5–43-cm interval. Bulk SAR is not determined at the 1387-m station. The trend of the bulk SAR with water depth results in an estimate of 10–100 $\text{g m}^{-2} \text{ yr}^{-1}$ (Van Weering et al., 2002). Sums of percentages are 107% (113 m), 98% (1387 m), 104% (396 m) and 109% (3097 m).

bound P (7–17%), organic P (3–12%), adsorbed P (2–9%), and detrital P (0–1%). The composition of the sedimentary P at the Iberian margin resembles more the sediments of the FOAM and Mississippi Delta sites studied by Ruttenberg and Berner (1993). The percentages of Fe-bound P and detrital P at the Iberian margin are very similar to those of the Mississippi Delta, whereas the percentage organic P is higher in our sediments and that of authigenic P lower than at the FOAM and Mississippi Delta sites (Ruttenberg and Berner, 1993). Long-term sinks of reactive P may involve organic P, Fe-bound P and authigenic P (Berner et al., 1993; Ruttenberg and Berner, 1993; Ingall et al., 1990; Slomp et al., 1996a). For the calculation of P budgets the burial of reactive P should be considered, because this fraction is potentially bio-available P, in contrast to detrital P (Ruttenberg, 1993). Filippelli (1997) compiled data from several margins and estimated that the total P accumulation rates for continental margins range between 0.9 and 80 $\text{mmol P m}^{-2} \text{ yr}^{-1}$. Total P burial rates of between 1.6 and 16 $\text{mmol P m}^{-2} \text{ yr}^{-1}$ are reported for the deep troughs of the Gulf of St. Lawrence (Louchouart et al., 1997). These are maximum values for reactive P, with the actual value being perhaps up to 50% lower, because continental margin sediments can have detrital P contents of 15% to over 40% of the total (Ruttenberg, 1993; Filippelli, 1997). Based on estimated P burial rates using the bulk sediment accumulation rate (Van Weering et al., 2002) and the solid-phase P concentrations (Table 2), our values for the Iberian shelf and slope are

well within the range for continental margin sediments. The canyon P accumulation rate, however, exceeds that estimate and is an order of magnitude higher. Differences in phosphorus burial rates are primarily caused by differences in the bulk sediment accumulation rate at our sites, just as they are in other environments (Filippelli, 1997). The P burial efficiency, calculated from $(\text{burial rate}/(\text{burial rate} + \text{efflux})) \times 100\%$, is smallest at the slope station, reasonably high at both shelf stations and extremely high at the canyon station (Table 3). Ingall and Jahnke (1994) showed evidence for enhanced P regeneration in sediments overlain by oxygen-depleted waters. Total P burial efficiencies of sediments overlain by oxygenated waters of ~13–55% were reported for the margins of North Carolina and California (Ingall and Jahnke, 1994). Reactive P burial efficiencies of ~46–74% were estimated in sediments from the Arabian Sea, excluding those sediments located in the oxygen minimum zone (bottom water oxygen concentration $< 2 \mu\text{M}$) (Schenau, 1999). Thus, the burial efficiency calculated for the canyon station is very high. The P burial efficiency increases with increasing bulk sediment accumulation rate. Similarly, the sedimentation rate was found to be the master variable for the organic carbon burial efficiency (Epping et al., (2002)). The suggested factors controlling organic carbon preservation are sorptive preservation, oxygen exposure time or otherwise. The P burial efficiencies (Table 3) are much higher than the organic C burial efficiencies (0.6–48%), which can be due to efficient re-incorporation of released

Table 3
Burial efficiency

Water depth (m)	Total P burial (mmol m ⁻² day ⁻¹)	Diff. HPO ₄ ²⁻ efflux (mmol m ⁻² day ⁻¹)	Burial efficiency (%)	In situ HPO ₄ ²⁻ efflux (mmol m ⁻² day ⁻¹)	Burial efficiency (%)
113	0.038	0.023	63	0.006 ± 0.001	86
1387	~0.001–0.005	0.019	3–20	0.015 ± 0.008	4–24
396	0.028	0.015	65	–	–
3097	0.589	0.015	97	–0.012 ± 0.032	97–100

Diffusive phosphate efflux is calculated with Fick's first law from the concentration gradient between the first sediment interval and the overlying water. The diffusion coefficient is corrected for temperature and tortuosity (Boudreau, 1997). E. Epping kindly provided phosphate pore water and overlying water concentrations and the in situ phosphate efflux ($n=3$) obtained during in situ experiments with the benthic lander, TROL (Epping et al., 2002). The TROL was not deployed at the 396-m station.

phosphate by the phosphorus-limited benthic community and to sorption onto Fe oxides in the oxic layer.

Epping et al. (2002) found a large discrepancy between estimated organic carbon delivery and total organic carbon deposition on the shelf. In the absence of offshore depocenters, this suggests that canyons are quantitatively important in focusing and burying shelf-derived organic matter (Epping et al., 2002). The impact on the global P budget is difficult to assess from only one site in the canyon. Deeper than 5 m in a piston core retrieved from the same canyon site, the sediment becomes more sandy/silty indicating a different sedimentation regime. Thus, there were apparently ~333 years of relative quiet conditions after the last great canyon flushing event (H. de Stigter, personal communication). The present study demonstrates the potential of canyons to act as a sink for reactive P phases.

6. Conclusions

The Iberian shelf stations represent contrasting depositional environments, but their P burial rates are very similar. The total P burial rate is smallest on the slope. The depositional site at the base of the Nazaré canyon is the only station where ongoing formation of authigenic CFA is suggested to occur, presumably because organic matter decomposition and Fe reduction occur relatively deep in the sediment of this station. The high organic matter deposition flux in the canyon stimulates both organic matter degradation and Fe

reduction rates resulting in the necessary build-up of phosphate in the pore water. We propose that local deposition areas such as occur at the lower part of canyons may be key sites for reactive P burial in the global ocean.

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