



## Phosphorus cycling in marine sediments from the continental margin off Namibia

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### ABSTRACT

In this study we investigate benthic phosphorus cycling in recent continental margin sediments at three sites off the Namibian coastal upwelling area. Examination of the sediments reveals that organic and biogenic phosphorus are the major P-containing phases preserved. High  $C_{org}/P_{org}$  ratios just at the sediment surface suggest that the preferential regeneration of phosphorus relative to that of organic carbon has either already occurred on the suspension load or that the organic matter deposited at these sites is already rather refractory. Release of phosphate in the course of benthic microbial organic matter degradation cannot be identified as the dominating process within the observed internal benthic phosphorus cycle. Dissolved phosphate and iron in the pore water are closely coupled, showing high concentrations below the oxygenated surface layer of the sediments and low concentrations at the sediment–water interface. The abundant presence of Fe(III)-bound phosphorus in the sediments document the co-precipitation of both constituents as P-containing iron (oxyhydr)oxides. However, highly dissolved phosphate concentrations in pore waters cannot be explained, neither by simple mass balance calculations nor by the application of an established computer model. Under the assumption of steady state conditions, phosphate release rates are too high as to be balanced with a solid phase reservoir. This discrepancy points to an apparent lack of solid phase phosphorus at sediment depth where suboxic conditions prevail. We assume that the known, active, fast and episodic particle mixing by burrowing macrobenthic organisms could repeatedly provide the microbially catalyzed processes of iron reduction with authigenic iron (oxyhydr)oxides from the oxic surface sediments. Accordingly, a multiple internal cycling of phosphate and iron would result before both elements are buried below the iron reduction zone.

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### 1. Introduction

Phosphorus (P) is one of the essential elements for life on Earth and plays an important role in the biological productivity in oceans and on continents. Because of the close relation between oceanic productivity and atmospheric CO<sub>2</sub>, changes in the oceanic P-cycle may considerably affect the chemistry of the oceans and atmosphere throughout geological time (e.g. Van Cappellen and Ingall, 1994, 1996). The major initial input into the oceans is by riverine transport of organic and inorganic P compounds (Benitez-Nelson, 2000). A great portion of this P is trapped in estuarine and coastal shelf areas and does not reach the open ocean (Ruttenberg, 1993). Paytan and McLaughlin (2007) estimated that almost 99% of particulate and 25% of dissolved P are buried in coastal shelf zones. The remaining particulate and dissolved P is exported to the deep ocean. During this transport the predominant portion of P, which is associated with organic substances is decomposed microbially within the water

column (Heggie et al., 1990; Baturin, 2003; Paytan and McLaughlin, 2007). As a result, P is released and subject to transformation processes (biological recycling, ad-, desorption) between dissolved and particulate phases (Faul et al., 2005). However, a small proportion of the P becomes buried into the sediment as altered organic compounds and as detrital and amorphous P mineral phases, adsorbed to particle surfaces (e.g. clay minerals) or iron (oxyhydr)oxides, or is transformed in situ into a mineralized form (various authigenic apatites) (Froelich, 1988; Compton et al., 2000; Paytan and McLaughlin, 2007). After burial, the behaviour of P is controlled by a number of biogeochemical processes. Release of phosphate to pore waters can result from: (1) microbial degradation of organic matter (Ingall et al., 1993; Jensen et al., 1995; Canfield et al., 2005); (2) by polyphosphate accumulating bacterial species (Schulz and Schulz, 2005; Diaz et al., 2008); (3) desorption from iron (oxyhydr)oxides when iron reduction takes place (e.g. Froelich et al., 1982; Baturin, 2003; Paytan and McLaughlin, 2007) and (4) dissolution of P-containing mineral forms during subsequent alteration (Suess, 1981; Froelich et al., 1988; Schenau and De Lange, 2001; Baturin and Dubinchuk, 2003). Under oxic conditions, phosphate concentrations in interstitial waters are predominantly controlled by a complex interplay of the release from

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organic debris, metabolic uptake, adsorption onto particle surfaces and diffusive transport. Furthermore, bioturbative transport processes can induce a permanent internal cycling (dissolution–reprecipitation) of particulate iron-phosphate phases within the oxidized and reduced sediment layer (Slomp and Van Raaphorst, 1993). Under sub- to anoxic conditions dissolved phosphate may continue to originate from the decomposition of organic substances, but may also be released from iron (oxyhydr)oxides when iron reduction takes place. However, assuming steady state, the accumulation of particulate P and release of phosphate into pore and bottom waters should be balanced by the burial rate of P in the sediment.

The shelf area off Namibia, as well as off Chile/Peru, belongs to the most productive systems in the modern ocean, where strong upwelling of nutrient-rich waters causes high primary production in surface waters, which sustain large zooplankton and pelagic fish stocks on the continental margin. Additionally, continental margin sediments are the main repository for remineralized marine organic carbon and a primary sink for phosphate (Ruttenberg, 1993; Filippelli, 1997). So, the high availability of organic material and the resulting very intense benthic activity make coastal high productive areas very suitable for investigations on the benthic P-cycle. Surface sediments of these shelf areas have previously been described as having favourable conditions for recent authigenic apatite formation (Burnett, 1977; Calvert and Price, 1983; Froelich et al., 1988; Glenn and Arthur, 1988; Bremner and Rogers, 1990; Borchers et al., 2005; Schulz and Schulz, 2005; Arning et al., 2008). Apart from impermeable hardgrounds where phosphogenesis can also occur, an increase of pore water phosphate is discussed as a prerequisite for the precipitation of authigenic apatite (e.g. Ingall and Jahnke, 1997; Canfield et al., 2005; Paytan and McLaughlin, 2007; Diaz et al., 2008). Moreover, Schulz and Schulz (2005) have found indications that the alteration between oxic and anoxic conditions in bottom waters and sediments in particular off Namibia is responsible for the redox-sensitive microbial formation and remineralization of polyphosphates (i.e. by *Thiomargarita namibiensis*).

Despite the aforementioned suitable conditions for phosphogenesis in shelf sediments, we investigate sampling sites without any evidence for active and ongoing precipitation of authigenic apatite. In this study we therefore focus on the benthic phosphorus cycle in continental margin sediments at three locations off the coast of Namibia under consideration of (1) the speciation of sedimentary P in continental margin surface sediments in a high productivity region with oxygenated bottom waters, (2) the comparison of distributions of P species with concentration profiles of interstitial waters, (3) obtaining a further insight into the sources and sinks of particulate P and (4) the interpretation and quantification of processes determining the distribution and behaviour of P. For the last, a model was used which has been developed by Slomp et al. (1996).

## 2. Location and oceanic environment

Sediment sampling has been carried out during the *RV Meteor* cruise M34/2 (Schulz et al., 1996) along the Namibian coastal region. The upwelling area off Namibia is regarded as the most productive of the four major eastern boundary systems on Earth (Benguela Upwelling System; Bianchi et al., 1999). Intense marine productivity is induced by the persistent SE trade wind field, which drives surface waters offshore and causes the upwelling of the nutrient-rich South Atlantic Central Water in at least four major cells. Due to seasonality in wind force, these cells show seasonal patterns with a corresponding change of the geochemical conditions in bottom waters (Shannon and Nelson, 1996). As a result, coastal sediments are enriched in organic substances. A number of studies has described sediments in this area as mainly consisting of organic-rich, marine, calcareous facies (i.e. foraminifers and coccoliths), barely diluted by terrigenous material (Calvert and Price, 1983; Bremner and Willis, 1993; Wefer et al., 1998). But, the offshore extension of phytoplankton filaments, lateral

particle advection in the water column, and redistribution of re-suspended particulate organic matter, lead to high total organic carbon contents in upper margin sediments as well. A reflection of these processes is a distinct depocenter of organic-rich sediments between 600 and 1500 m water depth, centered at about 25.5 °S (cf. Fig. 1; Inthorn et al., 2006; Mollenhauer et al., 2007).

## 3. Materials and methods

### 3.1. Sampling

Analytical work was done on material that has been recovered from about 1300 m water depth at three locations along the continental margin off Namibia (Fig. 1, Table 1). Sediment was sampled using a multi-corer. Sediments retrieved in this area are of Holocene age (Mollenhauer et al., 2002). Cores were transferred to the refrigerated on-board laboratory immediately after recovery and were processed at a temperature of about 4 °C. Overlying bottom waters were sampled, filtered and stored for analysis. For pressure filtration under argon atmosphere (5 bar), Teflon- and PE-squeezers and 0.2 µm cellulose acetate filters were used to collect the pore water. Sub-sampling for further solid phase investigations was done at every 0.5 cm (top 0–3 cm of the core), 1 cm (between 3 and 5 cm) and 5 cm (below 5 cm).

### 3.2. Pore water analyses

Onboard *RV Meteor*, pore water phosphate, ferrous iron and nitrate were measured photometrically immediately after pore water sampling, with an autoanalyzer using standard methods (Strickland and Parsons, 1968; Grasshoff et al., 1983; Schulz, 2006). In situ determination of dissolved oxygen in pore water was carried out using microelectrodes (Wefer et al., 1997).

### 3.3. Solid phase analyses

Bulk concentrations of trace elements (P and iron (Fe)) were determined by total digestion of 50 mg dried and ground sample in a HNO<sub>3</sub> (65%), HCl (30%) and HF (47–51%) mixture using a Microwave system (Zabel et al., 1999; Schulz, 2006). Dissolved element concentrations were measured using an inductively coupled plasma atomic emission spectrometer ICP-OES (Perkin Elmer Optima 3000). Application of standard reference material assured the accuracy of measurements; the precision was better than 5%.

The speciation of sedimentary phosphorus in the sediments was determined using a five-step sequential extraction scheme, where ~125 mg of dried and ground sediment sample was successively washed with 25 ml (1) 2 M NH<sub>4</sub>Cl (pH 7; 10 times at 4 h), (2) citrate dithionite buffer (pH 7.5; 8 h), (3) 1 M sodium acetate buffer (pH 4; 6 h), (4) 1 M HCl (24 h), and (5) 1 M HCl (24 h) after ignition at 550 °C (2 h) (Table 2). After steps (2) and (3) the samples were rinsed repeatedly with 25 ml 2 M NH<sub>4</sub>Cl and 25 ml demineralized water (2 h) to prevent the readsorption of phosphate. In addition, to test if a significant portion of total extractable P is exchangeable or loosely sorbed, we extracted ~125 mg of a sub-sample with 25 ml 0.35 M NaCl ((1b); 2 h). The extraction analysis is in accordance with the scheme of Ruttenberg (1992), and the modification of step (1) by Schenau and De Lange (2000) (Table 2). P concentrations in extraction solutions were measured photometrically (Perkin Elmer 550SE Spectrophotometer). Solutes from step (1) were measured for P and calcium and solutes from step (2) for P and Fe using an inductively coupled plasma atomic emission spectrometer ICP-OES (Perkin Elmer Optima 3000). Precision was generally better than 5%, except for step (2) (3–15%).

Biogenic apatite (i.e. hydroxyapatite in bones, scales, shells; biogenic debris) is soluble with NH<sub>4</sub>Cl extraction once all soluble

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