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Phosphorus accumulation associated with intense diagenetic metal-oxide cycling in sediments along the eastern continental margin of India

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Sequential phosphorus extractions were carried out to understand phosphorus cycling and enrichment in surface sediments along the eastern continental margin of India. Phosphorus associated with authigenic (P_{aut}) and biogenic (P_{bio}) phases is high by a factor of 2–10 in the continental shelf sediments compared to slope and deep-sea sediments. Phosphorus associated with Fe oxides (P_{Fe}) is enriched by a factor of 2–5 in the continental slope and rise sediments (500–3000 m water depth) compared to shelf sediments. Fe–Mn oxy(hydroxides) formed during early diagenesis adsorb phosphate from the water column or pore waters, thereby enriching the P_{Fe} fraction in the continental slope sediments. These results are in contrast with those from the Arabian Sea, where wide and intense mid-depth oxygen minimum zone (150–1200 m water depth) releases P_{Fe} to pore waters and enhances P_{aut} accumulation in the continental slope sediments.

Keywords: Early diagenesis, metal-oxide cycling, phosphorus accumulation, surface sediments.

PHOSPHORUS (P), an essential nutrient for life in the terrestrial and aquatic environment, is thought to control marine productivity on geological timescales[1]. Continental weathering is the most significant source of P to the oceans and is transported mainly by rivers in particulate and dissolved forms[2,3]. The dissolved phosphorus forms are utilized by phytoplankton and subsequently released to the water column during organic matter regeneration. A part of the dissolved phosphate transforms to particulate form during biogeochemical processes in the oceanic environment. The particulate P also occurs in apatite and other minerals, and is generally not involved in biogeochemical processes. However, clay particles with coatings of Fe–Mn oxy(hydroxides) have high capacity to adsorb phosphate from freshwater. It has been shown that phosphate desorption from clay minerals is nearly 2–5 times high due to buffering when compared to dissolved phosphate load entering into the ocean via rivers[4].

Sediments are the main sink for authigenic P which occurs mainly as a mineral, carbonate flourapatite (CFA). CFA formation is predominant in sediments from shallow water depths and continental slope sediments experiencing coastal upwelling[5–9]. In oceanic sediments P is associated

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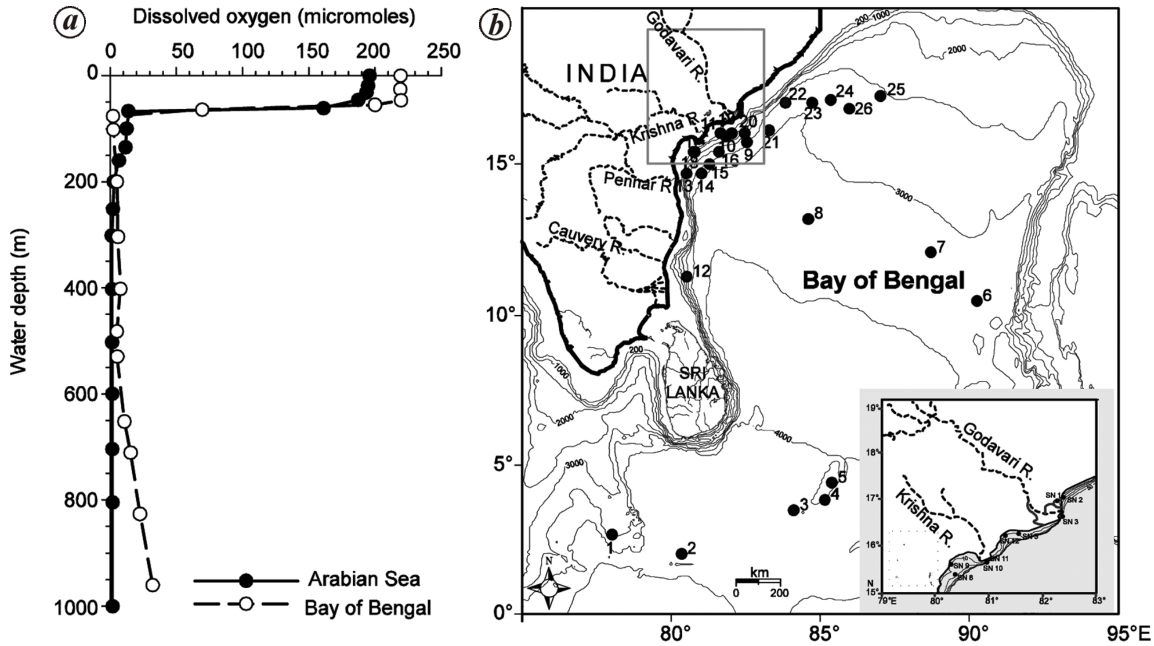

Figure 1. ***a***, Vertical dissolved oxygen profiles in the Arabian Sea and the Bay of Bengal (re-drawn after Naqvi[38]). ***b***, Map showing the location of stations with depth contours (m). (Inset) Sediment sampling along the continental shelf.

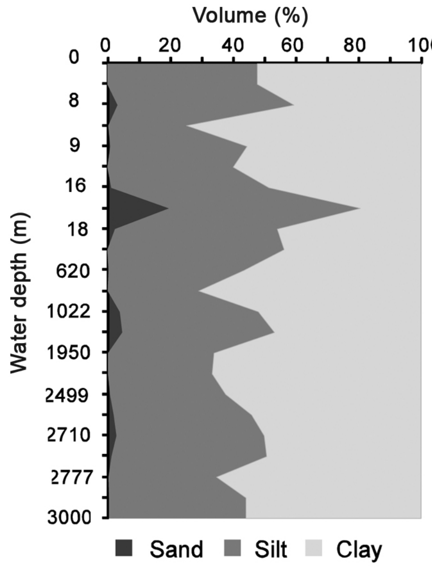

Figure 2. Textural variations along the continental shelf, slope and rise. Notice the near-uniform, fine-sized silty clay sediments with low sand percentage in the study area.

with several phases, viz. organic matter, adsorption to Fe–Mn (oxy)hydroxides, loosely-bound, fish debris and lattice-held apatite. The phosphorus associated with organic matter and Fe–Mn oxy(hydroxides) is reactive, while lattice-held phosphorus is not involved in biogeochemical processes. The burial of reactive P in oceanic sediments is a temporary phase, as these forms tend to redistribute to other phases during early diagenesis. Phosphate is released to pore waters during organic matter degradation, reduction of Fe–Mn (oxy)hydroxides and dissolution of fish debris[5,8–14]. The pore waters on saturation precipitate as CFA, a final burial phase of P in oceanic sediments. The various phases of P can be studied with speciation analysis which has the advantage of characterizing various forms of P when compared to bulk analysis.

The Bay of Bengal is one of the few areas in the world where Mn enrichment and ferromanganese micronodules from shallow water depths have been reported[15–17]. In this region the foraminifera carbonate productivity is low due to strongly stratified surface layer[18,19]. The upper slope sediments between water depths 150 and 500 m are also overlain by the oxygen minimum zone (OMZ), (Figure 1 *a*). We have studied the phosphorus cycling, spatial variations, transformation and burial phases in these oceanographic settings. Earlier only ancient phosphorites were reported in the continental shelf and slope sediments off Chennai[20,21]. Here we have undertaken sequential speciation experiments to distinguish various phases of P delivery and burial in the Bay of Bengal sediments.

Twenty-six core top sediments (0–2 cm) retrieved from continental slope, rise and deep sea (>400–4600 m water depth; Figure 1 *b*) along the eastern continental margin of India, collected during various cruises of *ORV Sagar Kanya 157* (September–October 2000) and *187* (January–February 2003) were selected for the present study. In addition, nine surface sediments collected using the Peterson grab from a fishing boat along the eastern Indian continental shelf (<20 m water depth; Figure 1 *b*) were also selected. After sampling, the sediment samples were

Table 1. Sample position details and concentration of various phases of phosphorus (ppm). The stations in bold letters are retrieved from topographic highs

					ppm					
Stn. no.	Stn. ID	Depth (m)	Latitude (N)	Longitude (E)	P_{bio}	P_{Fe}	P_{aut}	P_{det}	P_{org}	P_{total}
Continental margin sediments										
1	**SK 157/5[b]**	**2972**	**2.669**	**78.006**	**141**	**22**	**87**	**17**	**35**	**302**
2	SK 157/6[a]	4458	2.0189	80.341	149	81	n.d	59	102	391
3	SK 157/7[a]	4197	3.4851	84.111	110	115	41	62	82	410
4	**SK 157/9[a]**	**3568**	**3.8491**	**85.158**	**110**	**14**	**40**	**16**	**29**	**209**
5	**SK 157/12[a]**	**3439**	**4.4066**	**85.386**	**110**	**17**	**107**	**12**	**31**	**277**
6	SK 157/17[a]	3220	10.516	90.255	110	56	54	54	82	356
7	SK 157/20[a]	3202	12.147	88.711	73	54	43	42	70	282
8	SK 157/23[a]	3260	13.227	84.603	91	62	57	49	150	408
9	SK 157/26[a]	2499	15.786	82.489	67	106	33	87	132	424
10	SK 157/28[a]	1022	15.913	81.832	30	142	33	108	171	485
11	SK 157/29[a]	620	16.03	81.665	12	231	57	132	126	558
12	SK 187/9[c]	1950	11.316	80.52	110	76	27	73	146	432
13	SK 187/17[c]	1852	14.681	80.508	102	126	40	135	117	520
14	SK 187/18[a]	2777	14.736	81.023	55	116	43	87	115	415
15	SK 187/19[c]	2686	14.982	81.275	71	188	33	163	100	555
16	SK 187/20[a]	2355	15.363	81.602	24	142	38	94	153	451
17	SK 187/21[c]	483	15.381	80.753	78	252	20	175	137	662
18	SK 187/21[a]	926	15.351	80.794	24	113	29	134	146	446
19	SK 187/23[a]	959	16.042	82.035	24	147	29	110	133	443
20	SK 187/24[c]	1945	16.039	82.474	78	225	35	161	137	636
21	SK 187/25[c]	2868	16.082	83.283	80	138	34	97	131	480
22	SK 187/27[c]	2645	17.03	83.741	37	69	24	74	188	391
23	SK 187/28[c]	2829	17.022	84.47	43	82	33	65	222	446
24	SK 187/29[c]	2710	17.063	85.15	37	90	43	70	172	412
25	SK 187/30[a]	2579	17.093	86.752	43	118	24	76	110	370
26	SK 187/33[c]	2729	16.754	85.981	49	41	33	72	128	324
Shelf sediments										
1	SN-1	5	16.912	82.263	243	85	241	195	228	991
2	SN-2	16	16.917	82.388	166	72	281	199	125	843
3	SN-3	17	16.608	82.374	166	35	248	152	115	716
4	SN-5	8	16.387	81.98	134	69	301	139	228	870
5	SN-8	18	15.617	80.832	153	48	335	160	127	823
6	SN-9	8	15.675	80.833	147	70	361	123	115	817
7	SN-10	18	15.884	81.225	147	80	328	218	140	912
8	SN-11	12	15.942	81.2	147	95	368	139	214	962
9	SN-12	9	16.28	81.635	185	74	375	123	199	956

n.d. Not determined; [a]Gravity core; [b]Spade core; [c]Piston (pilot) core.

transferred under cold conditions and stored at 4°C in cold repository till further laboratory analysis. Representative portions of the samples were dried in hot-air oven at 60°C, powdered using an agate mortar and pestle, homogenized and stored in air-tight plastic vials until further analysis. Table 1 provides the sampling details and analytical results. Complete analytical protocol of P speciation modified by Schenau *et al.*[14], and adopted by Prakash Babu and Nagender Nath[8] for the eastern Arabian Sea sediments provides in-depth details of speciation experiments followed in this study. The grain size was determined after removing carbonate and organic matter using Malvern laser particle size analyzer (Master sizer 2000) in a few selected samples.

Texturally, the sediments are mainly silty clay in the continental shelf, slope and rise (Figure 2). The shelf sediments have high P_{aut} (P associated with authigenic phase) and P_{bio} (P associated with biogenic phase) concentration (147–375 ppm) compared to continental slope and continental rise sediments (12–149 ppm; Figure 3 and Table 1). P_{Fe} concentration, on the other hand, is higher (41–252 ppm) in the continental slope and rise sediments compared to shelf sediments (33–95 ppm; Figure 3). High P_{Fe} concentration (100–252 ppm) is restricted to sediments below the OMZ (Figures 3 and 4). The processes leading to enrichment of P_{Fe} content in the slope and rise sediments are discussed below.

The shelf sediments with high terrigenous input are sites for P burial. P sequestration as P_{aut} is observed in several continental margin sediments, viz. Gulf of St Lawrence, the eastern Canadian shelf and slope, the Chesapeake Bay, the Portuguese continental margin

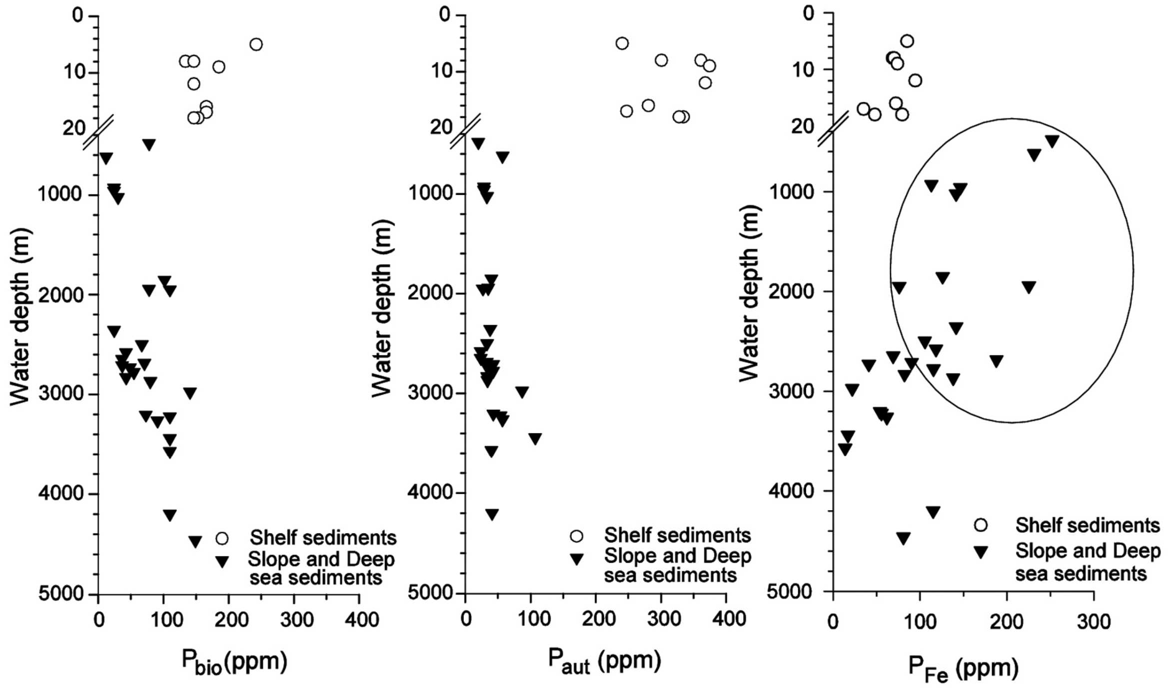

Figure 3. Concentration of phosphorus associated with biogenic (P_{bio}), authigenic (P_{aut}) and iron (P_{Fe}) fractions versus water depth in the study area. Notice high P_{Fe} concentration between 500 and 3000 m water depth.

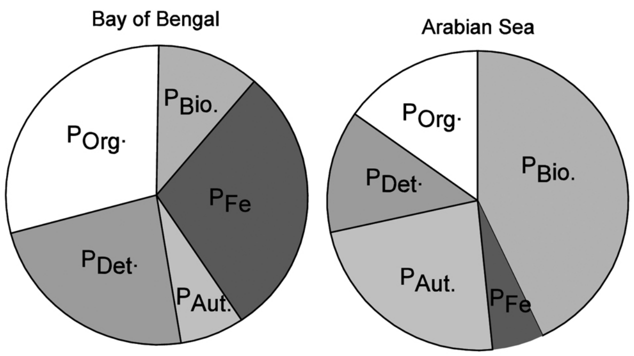

Figure 4. Percentage variations of different fractions of phosphorus along the continental upper slope, lower slope and rise (n = 18) sediments in the Bay of Bengal (present study). Also included for comparison are the continental slope and rise data[8] in the Arabian Sea. Notice high P_{Fe} and P_{Org} and high P_{Bio} and P_{Aut} fractions in slope sediments of the Bay of Bengal and Arabian Sea respectively.

sediments, Long Island Sound and Mississippi Delta which experience high terrigenous input[11,22]. The Bay of Bengal shelf sediments with high terrigenous input from several peninsular Indian rivers are also the sites for P burial as P_{aut}, similar to other continental shelf sediments. The shelf sediments with high sedimentation rates are also sites for biogenic apatite accumulation (P_{bio})[23]. The biogenic apatite represents P associated with fish bone, scale and teeth accumulation. The biogenic apatite accumulation in the Bay of Bengal shelf sediments is due to shorter transit period in the water column, high sedimentation and reducing conditions either in pore water or close to the sediment–sea water interface The preservation of biogenic apatite under low dissolved oxygen concentrations is well established[8,10,23–25]. Low P_{Fe} concentration in the Bay of Bengal shelf sediments also supports the same.

P_{Fe} surprisingly is enriched below the OMZ in continental slope sediments of the Bay of Bengal (Figure 3). Fine-sized silty clay sediments from the continental shelf to rise infer that texture is not a factor for P cycling. Diagenetic recycling of metal oxides and the adsorption of P by metal oxides seem to enrich the P_{Fe} fraction in the Bay of Bengal. High fluvial and clastic sediments, and rapid removal of organic matter by settling lithogenic material (ballast effect) enhances burial of labile organic matter in the study area. The presence of hydrolysable organic compounds indicates lower exposure time for dissolved oxygen, rapid burial of sedimentary labile organic carbon[26–30], consumption of dissolved oxygen within the upper few centimetres in the sediment column and development of reducing conditions close to the interface. In addition, the fine-sized sediments, low porosity and less foraminifera carbonate productivity[17,19,31] limit diffusion of dissolved oxygen. These reducing conditions keep in pace with high sedimentation by being close to the interface. The continuous movement of reducing conditions with sedimentation remobilizes elements associated with organic matter and metal oxides, and diagenetically enriches several major and trace elements. High sulphate reduction rates (sulphate consumption) also reiterate the extent of organic matter oxidation and the associated diagenetic processes in the Bay of Bengal compared to the Arabian Sea[32].

The Fe-oxides which are utilized for organic matter degradation release reduced Fe and P to pore waters from Fe-reduction zone[33]. Both Fe and P diffuse towards the sediment surface. Due to oxygenated interface the reduced fraction of Fe^{2+} precipitates as Fe-oxy (hydroxides), which adsorb pore water HPO_4^{2-} diffusing upwards[7,12,34–36]. Fe-oxy (hydroxides) have large surface area which adsorbs phosphate from the water column and/or pore waters[7,37]. With successive sedimentation, the Fe-oxy (hydroxides) along with adsorbed phosphate are buried and transferred to the Fe-reduction zone. This zone keeps in phase with sedimentation by remaining close to the interface. In the Fe-reduction zone again Fe-oxy (hydroxides) are reduced, release Fe^{2+} and associated P again to pore waters, and diffuse towards the sediment surface. The diagenetic enrichment of P_{Fe} in continental slope and rise sediments coincides with high Mn concentration and Fe–Mn micronodules in the study area[15]. The formation of ferromanganese micronodules in shallow water is a unique process in the Bay of Bengal. High Mn concentration in this region was explained in terms of its rapid cycling due to faster burial, transfer to Mn-reduction zone, Mn dissolution, and upward diffusion and precipitation due to high consumption rates of oxygen[16,17]. Continuous remobilization and rapid cycling of P associated with Fe-oxides close to the sediment–sea water interface promote diagenetic enrichment of the P_{Fe} fraction in the study area (Figure 4). On the other hand, P_{Fe} is released to pore water due to wide and intense mid-depth OMZ in the Arabian Sea. Due to dissolution of Fe (oxy)hydroxides in sediments underlying the OMZ[33], the dissolved phosphate either accumulates in pore waters or diffuses to the overlying water column. The pore-water-dissolved phosphate upon reaching saturation precipitates as solid phase P_{aut} mineral, CFA. The transformation of labile phases of P to solid phase CFA which enhances P-burial in continental slope sediments with varying dissolved oxygen concentrations from the Arabian Sea (Figure 4) has been explained earlier[8].

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Estimation of geomorphic threshold in permanent gullies of lateritic terrain in Birbhum, West Bengal, India

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The present geomorphic study focusses on predicting threshold conditions and vulnerable locations where gully heads might develop in the lateritic terrain, located at the eastern plateau fringe of Rajmahal Basalt Traps, Birbhum, West Bengal, India. The modern concept of geomorphic threshold is applied here on gully erosion hazard to identify the critical slope of gully head (*S*) and upstream drainage area (*A*) with a core relationship of $S = aA^{-b}$. Based on 118 gully heads we have statistically derived significant relationships between slope and drainage area ($r = -0.55$); overland flow (*Q*) and slope length (*L*; $r = 0.694$); relative shear stress (τ) and slope ($r = 0.915$); as well as overland flow detachment rate (*H*) and eroding force of overland flow (*F*; $r = 0.980$). The established *S–A* critical relationship, as geomorphic threshold, is expressed as $S = 17.419A^{-0.2517}$, above which gully initiation occurred on the laterites. This equation can be used as a predictive model to locate the vulnerable un-trenched slopes (i.e. potential gully erosion locations) in other lateritic areas of West Bengal. The constant *b* value (0.2517) and Montgomery-Dietrich envelope suggest a relative dominance of overland flow (52.51% of sample gully heads) in the erosion processes. The result of erosion model predicts an annual soil loss of 2.33–19.9 kg m^{-2} $year^{-1}$ due to overland flow above the gully heads.

Keywords: Geomorphic threshold, gully, laterite, overland flow.

SOIL erosion is an issue where the adage 'think globally, act locally', is clearly applicable. Land degradation due to soil erosion is a momentous hazard in India[1] and gully erosion (i.e. extreme form of accelerated soil erosion) already engulfs about 3.975 million ha of land in India[2–4]. It is estimated that soil erosion takes place at the rate of 16.35 tonne ha^{-1} $year^{-1}$ in India, and about 29% of total eroded soil is lost permanently to sea and 10% is deposited in reservoirs[5–8].

Loss of soil is accelerated due to gully erosion which represents a major sediment producing process, generating between 10% and 95% of total sediment mass at catchment scale, whereas gully channels often occupy less than 5% of total catchment area[9–11]. A gully is defined as an

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