

# Distribution of phosphorus and phosphatisation along the western continental margin of India

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## Abstract

Phosphate content in the bulk sediments range from 0.02 to 2.17% and on carbonate free basis it varies from 0.03 to 6.57%. The partition studies indicate that contribution from the acid resistant detrital minerals (HCl insolubles) is negligible. In the inner shelf, the phosphorus is mainly associated with iron (as ferric-phosphate?) and organic carbon. In the outer shelf/slope its association with carbonate suggests its authigenic/diagenetic origin. This is also supported by X-ray diffraction studies wherein the apatite peak is revealed in some samples. In general, sympathetic relationship of phosphorus with organic carbon in the study region indicates genetic relationship between these two elements, which is an important condition for phosphatogenesis. Further, these studies suggest that the outershelf/slope region between Bombay and Quilon is the promising area for detailed exploration for phosphorite deposits.

## INTRODUCTION

Submarine phosphorite was first recognised among samples dredged from the Agulhas Plateau off South Africa by the *Challenger* Expedition in 1873 (Murray and Renard, 1891). In 1937, phosphorite nodules were found in samples from tops of submarine banks off Southern California (Dietz *et al.*, 1942). Subsequently, oceanographic expeditions have reported phosphorite nodules in many scattered localities off the coasts of several countries. Occurrence of these phosphorite nodules are known from nearshore to more than 300 km offshore, in water depths ranging from 20 m to more than 300 m but mostly in waters less than 400 m. These deposits are found to be in association with siliceous deposits (cherts, porcellanite and diatomite), carbonates, glauconite. Modern phosphorite formation has been reported off southwest African and Peru/Chile coasts (Veeh *et al.*, 1973; Manheim *et al.*, 1975; Baturin *et al.*, 1972; Burnett *et al.*, 1980; O'Brien and Veeh, 1980, 1983; Burnett *et al.*, 1983).

During the last few decades, these deposits have been an object of great interest from the point of view of their economic exploitation and the opportunity they offer to establish the environment and mode of formation of fossil phosphorites. Although considerable amount of prospecting has been undertaken in several areas, there has been no commercial phosphorite production offshore to date (McKelvey, 1967). While this is the position in regard to prospecting in so far as the scientific investigations are concerned, much progress has been made in understanding the chemical and mineralogical composition of these nodules. Although divergent views have been expressed by several scientific investigators who have tried to study the origin of these phosphorite nodules, some of these deposits occur in regions of intense upwelling and biological productivity, and in areas of low sedimentation. Since the western continental shelf of India is also subjected to intense seasonal upwelling, it has been considered appropriate to study in detail the environmental conditions suited for the formation of these deposits.

## REVIEW OF EARLIER WORK

Earlier report of phosphorite along western shelf is that of a specimen containing about 10%  $P_2O_5$  found in 1967 by a Russian Oceanographic Expedition at a sampling station in the slope region (200–300 m depth) off Quilon (Baturin, 1981). Radio carbon dates of this material ranged from 6500–33000 yrs. Murty *et al.* (1968) and Marching (1972) reported the distribution of phosphate in the core samples collected from a few transects across the continental margin between Alleppey, Bombay, Cochin and Karachi. Nair (1969) reported phosphatised ooids from the outershelf region between Bombay and Mangalore. Setty and Rao (1972) studied the distribution of phosphate in the cores collected from the shelf and slope regions off Saurashtra coast. Rao *et al.* (1978) studied the distribution of phosphate in the sediments of the northern half of the western continental shelf of India and suggested that the outershelf region between Gulf of Cambay and a little south of Bombay and the continental slope region are environmentally favourable for detailed exploration of phosphate. Recently, detailed surveys of the shelf region between Goa and Bombay, by echo-sounder, side-scan sonar and seismic profiling, have demarcated a series of well-defined ridges rising to a height of 2–5 m above the sea bed. These ridges are made of algal, coral and shell limestones and extend out from the clay-sand boundary at a depth of about 50 m to the shelf edge and have been traced over a distance of about 150 km along the shelf. Analysis of rocks sampled from these ridges showed that some contain up to 5% phosphate (Siddiquie *et al.*, 1984). In addition, some of the sediment samples collected from the nearby areas of these ridges between Ratnagiri and Goa are found to contain 5–6% of phosphate (Personal communication from Shri K. H. Vora). According to Nair (1985), who analysed seventeen rock samples containing algal and oolitic limestones recovered from depths ranging from 70–150 m on the western continental shelf from Saurashtra to Kerala, prominent apatite peak was present only in the algal limestones off Goa and  $P_2O_5$  concentration varied between 0.8 and 10.8% indicating wide variation in composition. Mud banks occurring in shallow waters (less than 20 m water depth) off the southwest coast of India are found to contain a few patches of sediments assaying 1–5% phosphate on dry basis and these finely divided muds are being used by the local people to improve local acid soils.

## SEDIMENTARY FRAMEWORK AND OCEANOGRAPHIC FEATURES OF WESTERN CONTINENTAL MARGIN

**Sedimentary framework**

Texturally, sediments of the western continental shelf of India exhibit a clear cut zonation (Stackelberg, 1972; Nair and Hashimi, 1980). The inner shelf region (from coast to 50 m water depth) is covered by modern silty clays or clayey silts up to Quilon, south of which are terrigenous sands. These are followed seaward by sands, silty sands and clayey sands in the outershelf region (50 to 150 m). On the contrary, the entire shelf region north of Gulf of Kutch is completely covered by fine-grained sediments. In the continental slope region, fine-grained sediments (olive-grey to green muds) are encountered up to a depth of about 1500 m beyond which brown muds occur. Topographically, the inner shelf region is smooth, while the outer shelf region is characterised by rugged topography with a system of ridges of 1 to 5 m in height trending NNE-SSW, almost parallel to the coastline. Radiocarbon ages of

sediments and rocks from outer shelf region are between 9000 and 12000 years B.P. (Nair, 1985).

Chemically, the inner shelf sediments are characterised by very low  $\text{CaCO}_3$ . The coarser sediments in the outer shelf region are associated with high  $\text{CaCO}_3$ , mostly contributed by skeletal and non-skeletal components. This distribution pattern is found to be characteristic of the region between Gulf of Kutch and Mangalore (Rao *et al.*, 1978; Rao, 1983). In the southern region, though sands occur in the outer shelf region as in the north, they differ chemically from the sands in the north, in that, they are mostly made up of quartz. In the slope region, carbonate content of the sediments is relatively low compared to carbonate content of the outer shelf region, in the region between Gulf of Kutch and Mangalore, while in the southern region, the reverse is the case. The high carbonate content recorded in the slope region in the southern region is not a continuous feature but occurs in patches (Paropkari, 1983). The sediments of the slope region are characterised by very high content of organic carbon (> 6%), those of the outer shelf region by lesser content (< 1.5%) and intermediate values are associated with inner shelf sediments (2–4%; Paropkari *et al.*, in press).

### Upwelling

The presence of upwelling along the western continental shelf of India during the southwest monsoon season is well documented (Banse, 1968; Sharma, 1968). These studies have indicated that there is a time lag in the occurrence of this phenomenon from south to north. While this phenomenon is well established between Cape Comorin and Bombay, not much information on the upwelling process in the shelf region north of Bombay is available.

### Biological productivity

As a consequence of seasonal upwelling biological productivity is also comparatively high. Primary productivity along western continental margin of India was studied at several stations during different seasons and an average annual picture of the column productivity of the waters was given by Qasim (1977). Broadly speaking, the area under study can be divided into 3 regions—high, medium and low, based upon the productivity values:

1. The area off Gulf of Kutch and the region off the southwest coast of India (from Calicut to southern tip of India) as a region of high productivity (0.75 to 1.0  $\text{gC/m}^2/\text{day}$ ).
2. Areas off Saurashtra coast and the region between Bombay and Ratnagiri and between Mangalore and Calicut as regions of medium productivity (0.5 to 0.75  $\text{gC/m}^2/\text{day}$ ).
3. Regions between Gulf of Kutch and Bombay and Ratnagiri and Mangalore as regions of low productivity (0.25 to 0.5  $\text{gC/m}^2/\text{day}$ ).

### Dissolved oxygen content

Considerable amount of data is available on the dissolved oxygen content of the waters along the western continental margin of India. The well mixed surface layer is characterized by high oxygen concentration and an abrupt decrease in dissolved oxygen occurs within the upper thermocline. Oxygen-deficient conditions

exist within a large body of water within the depth range 150–1000 m leading to reducing conditions particularly north of about 12°N latitude in the Arabian sea. (Sen Gupta and Naqvi, 1984). Thus, the outer shelf and slope sediments are permanently in contact with oxygen-deficient waters. Seasonal fluctuations in the thickness of isothermal layer may also expose the sediments of the innershelf to the oxygen-deficient layer during periods of upwelling.

#### MATERIALS AND METHODS

About 500 surficial sediment samples were collected from all over the shelf and parts of the slope region between Indus Canyon in the north and Cochin in the south along traverses roughly spaced at 20 km apart. In the region between Indus Canyon and Mangalore, sampling was carried out mostly between 20 and 250 m water depths and in the region between Mangalore and Cochin, it was carried out between 17 and 1020 m water depths. All the sampling was done using La Fond-Dietz snapper/Van Veen grab.

Representative samples were obtained from the collections made at each station and a suitable aliquot of each sample was digested with hydrofluoric and perchloric acids for determination of total phosphorus in the bulk samples. In order to understand the partition of phosphorus in the sediments, some sediment samples were leached with 10% acetic acid and 50% hot HCl. Determinations of phosphorus in the bulk samples as well as in the chemical leaches were carried out colorimetrically, following the method of Riley (1958). The aim of the partition studies carried out is to understand (1) the amount of phosphorus associated with carbonate phase, authigenic minerals, loosely sorbed ions and interstitial water evaporates soluble in acetic acid, and (2) phosphorus associated with everything including ferro-manganese oxide phases, iron oxide minerals excepting more resistant silicates and aluminosilicates insoluble in HCl. The precision of colorimetric analysis of both bulk samples and leached samples was better than 5% on the basis of duplicate analysis. The accuracy was checked by analysis of USGS rock standards BCR-1 and AGV-1. Since fractionation analysis was not carried out sequentially, the amount of phosphorus in each fraction was obtained by subtraction.

The data from all the three regions was subjected to statistical analysis and the interrelationships obtained between phosphate and other important elements of the sediments are given in the form of matrix (Table II). In addition, the data from the Ratnagiri-Mangalore and Mangalore to Cochin sectors were subjected to R-Mode factor analysis using the TDC-316 computer in order to understand the factors controlling the distribution of phosphorus in these sediments.

#### RESULTS

Figure 1 shows the areal distribution of  $P_2O_5$  in the surficial sediments of the western continental margin of India between Indus Canyon in the north and Cochin in the south. The ranges of phosphate content in the unconsolidated sediments on total sample and carbonate free basis, in the acetic acid and HCl leaches, acid insoluble residues and  $C_{org}/P_2O_5$  ratios for the inner shelf, outer shelf and slope regions of the three different sectors, i.e., Indus Canyon to Port Dabhol, Ratnagiri to Mangalore and Mangalore to Cochin, are given in Table I. Table II shows the interrelationships between phosphate and other elements like, Al, Fe, Mn, organic carbon

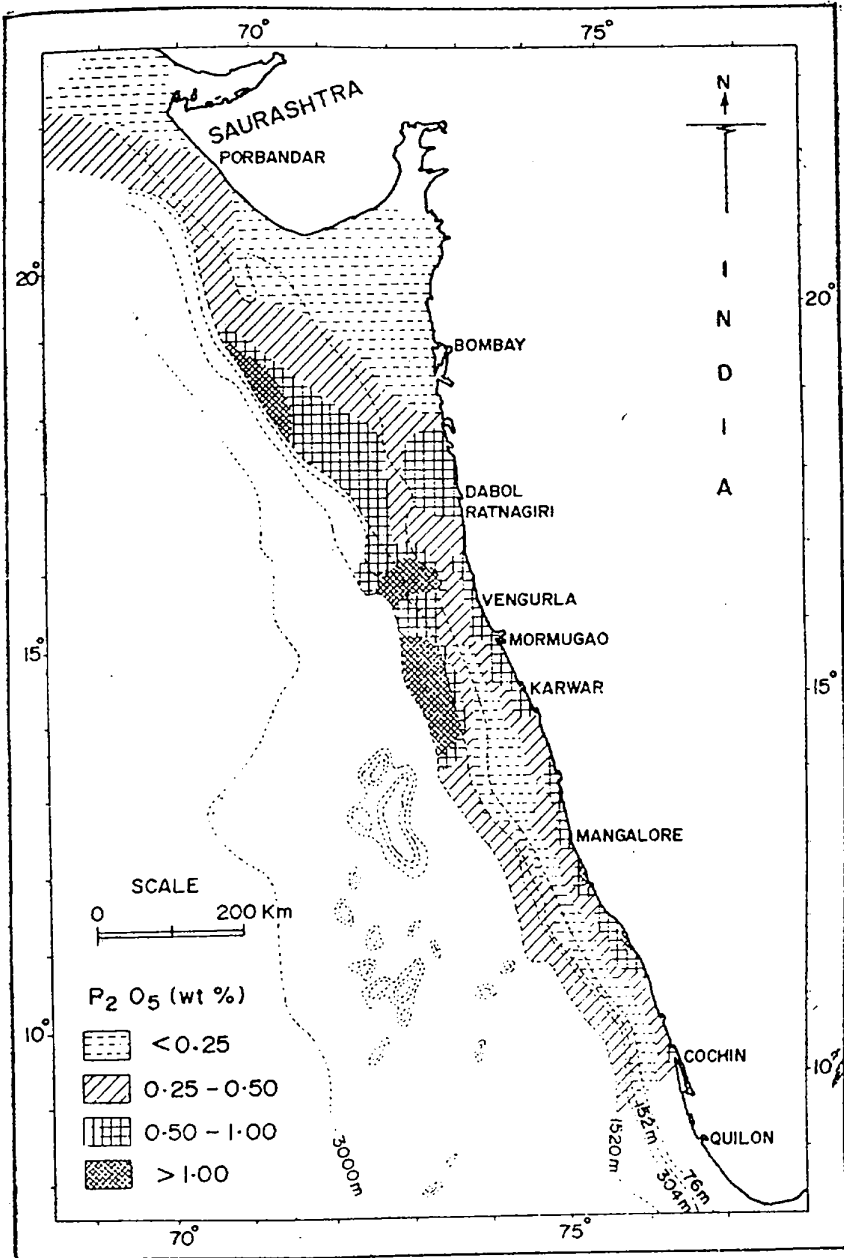


Figure 1. Distribution of  $P_2O_5$

TABLE I.

Area	Region	Bulk Sample	Acetic Acid Soluble Fraction	HCl Soluble Fraction	Acid Insoluble Fraction	C <sub>org</sub> /P <sub>2</sub> O <sub>5</sub> Ratios
(1)	(2)	(3)	(4)	(5)	(6)	(7)
Indus Canyon to Port Dabhol	Inner shelf	0.18 - 0.95 (0.19 - 1.00)	N.D.	0.12 - 0.20 (21.00 - 67.00)	0.16 - 0.70 (40.00 - 75.00)	6.0 - 13.0
	Outer shelf	0.17 - 1.20 (0.74 - 3.00)	N.D.	0.14 - 1.14 (82.00 - 95.00)	0.03 - 0.05 (15.00 - 30.00)	2.0 - 12.0
Ratnagiri to Mangalore	Inner shelf	0.25 - 0.75 (0.28 - 1.00)	0.02 - 0.26 (23.00 - 36.00)	0.5 - 0.44 (64.00 - 72.00)	0.05 - 0.18 (00.03 - 15.00)	6.0 - 19.0
	Outer shelf	0.09 - 1.53 (0.29 - 3.06)	0.02 - 0.95 (26.00 - 80.00)	0.05 - 0.28 (20.00 - 73.00)	0.20 - 0.30 (0.20 - 15.00)	1.5 - 16.0
	Slope	0.20 - 2.17 (1.05 - 6.57)	0.08 - 1.75 (63.00 - 82.00)	0.09 - 0.40 (16.00 - 32.00)	0.02 - 0.03 (0.70 - 15.00)	2.0 - 10.0
Mangalore to Cochin	Inner shelf	0.03 - 1.19 (0.04 - 1.53)	0.01 - 0.37 (7.41 - 94.54)	0.08 - 0.47 (0.00 - 68.88)	0.00 - 0.77 (0.00 - 87.17)	1.6 - 16.0
	Outer shelf	0.02 - 0.45 (0.03 - 1.28)	0.03 - 0.16 (10.52 - 100.00)	0.02 - 0.18 (0.00 - 80.00)	0.00 - 0.16 (0.00 - 57.00)	1.0 - 20.0
	Slope	0.26 - 0.54 (0.36 - 0.91)	0.06 - 0.17 (22.22 - 46.15)	0.03 - 0.23 (0.00 - 61.50)	0.01 - 0.31 (7.69 - 57.00)	2.0 - 36.0

A=All the values expressed in Columns 3 to 6 are in per cent.

B=Values given in brackets of Column 3 are on carbonate free basis.

C=Values given in brackets under Columns 4, 5 and 6 represent ranges of percentage contribution made by each fraction to the concentration in bulk sample.

and also CaCO<sub>3</sub>. From the data presented in Figure 1 and Tables I and II the following general observations can be made on the distribution of phosphate and to a certain extent on the manner of its incorporation into the sediments.

#### BULK SAMPLE GEOCHEMISTRY

##### Indus Canyon to Port Dabhol Region

(a) On the total sample basis, the phosphate content varies between 0.17 and 1.20% and on carbonate free basis between 0.19 and 3.00% (Table 1).

(b) Figure 1 shows that the entire shelf region off Gulf of Kutch and the inner shelf region between Gulf of Cambay and a little south of Bombay is characterised by very low values of phosphate content (0.25%) except for a small portion off Porbandar where the inner shelf region is characterised by high phosphate content (0.25 to 0.50%). In the outer shelf region, the calcareous relict sediments have a higher content of phosphate than the inner shelf sediments and further, the phosphate content shows an increasing trend towards the shelf edge especially between Bombay and Port Dabhol.

TABLE II.

Area	Region	Al	Fe	Mn	CaCO <sub>3</sub>	C <sub>org</sub>
Indus Canyon to Port Dabhol	Total samples (n=74)	-0.59	0.13	-0.63	0.62	0.30
	Inner shelf (n=40)	-0.85	0.47	-0.78	0.66	—
	Outer shelf (n=34)	—	—	—	—	—
P <sub>2</sub> O <sub>5</sub>  Ratnagiri to Mangalore	Total samples (n=220)	0.21	0.20	0.51	-0.28	0.79
	Inner shelf (n=119)	0.73	0.71	0.61	0.56	0.88
	Outer shelf (n=62)	—	—	—	—	0.73
	Upper slope (n=39)	—	—	0.33	—	0.87
	Total samples (n=136)	0.59	0.63	0.38	—	0.34
	Mangalore to Cochin	Inner shelf (n=52)	0.36	0.45	—	—
Outer shelf (n=59)		0.33	0.39	0.34	0.59	0.42
Upper slope (n=25)		—	—	—	—	—

(c) The black coloured oolites and shells and portions of the dredged limestones which have been analysed show phosphate ranging from 0.8 to 1.2% while the grey-coloured oolites, shells and limestones contain only 0.1 to 0.2% of phosphate.

(d) The C<sub>org</sub>/P<sub>2</sub>O<sub>5</sub> ratios in the sediments of the inner shelf region have lower range of variation than the ratios in the sediments of the outer shelf region (Table I).

(e) Statistical correlations show that phosphorus has a negative correlation with Al and Mn and a positive correlation with organic carbon and calcium carbonate when the complete northern region is considered. In the inner shelf region, phosphorus shows negative correlation with Al and Mn and positive correlation with Fe and calcium carbonate. It does not show any relationship with organic carbon. In the outer shelf region, it does not exhibit any relationship with any of the elements mentioned.

#### Ratnagiri to Mangalore Region

(a) In this region, the phosphate content ranges from 0.09 to 2.17% on the bulk sample basis and from 0.28 to 6.50% on carbonate free basis.

(b) In marked contrast to the northern region, the inner shelf region is characterised by higher ranges of phosphate content (0.25 to 0.50% and 0.5 to 1.0%). However, these two ranges of phosphate content occur as discontinuous patches alternating with each other. Further, the zone 0.25 to 0.50% extends into the outer shelf

up to Mormugao in the south, south of which the outer shelf sediments up to Mangalore have a lower content of phosphate (<0.25%). The outer shelf and slope region off Vengurla and the slope region between Mormugao and Karwar have patches of sediments having high phosphate content (>1%) separated by a zone of sediments in the range of 0.5 to 1.0%.

(c) The  $C_{\text{org}}/P_2O_5$  ratios vary widely in the outer shelf region as compared to the inner shelf and slope regions (Table I).

(d) In marked contrast to the interrelationships observed in the northern region, phosphate exhibits a positive correlation in this sector with all the elements except calcium carbonate with which it shows a negative correlation. Zone-wise, in the inner shelf region, the relationships obtained are similar to those obtained for the entire shelf region. In the outer shelf and slope it shows a significant positive correlation with organic carbon and a negative correlation with manganese only in the case of slope region.

### Mangalore to Cochin Region

(a) In this region, the phosphate ranges from 0.02 to 1.19% on the bulk sample basis and from 0.03 to 1.53% on the carbonate free basis.

(b) The distribution pattern of phosphorus in the inner shelf and outer shelf regions is more or less similar to that between Karwar and Mangalore while in the slope region, the phosphate content is uniformly in the range of 0.25 to 0.50% which is lower than that encountered in the two northern regions.

(c) The pattern of  $C_{\text{org}}/P_2O_5$  ratios are very much similar to that of Ratnagiri-Mangalore sector.

(d) On the total sample basis over the entire region, phosphorus bears a significant positive relationship with Al, Fe, Mn and organic carbon. Zone-wise, in the inner shelf region, it shows positive correlation with Al, Fe and organic carbon, in the slope, with none.

### PARTITION PATTERN OF PHOSPHATE

#### Acetic acid leaches

Determination of phosphorus in the acetic acid leaches have been made only on the sediments collected from the shelf region between Ratnagiri and Cochin and the ranges of phosphorus values obtained in the leaches from the two areas are given in Table I. The data presented shows that in Ratnagiri-Mangalore sector, highest range of values occur in the leaches of the continental slope, lowest range of values occur in the inner shelf region and values in the intermediate range in the outer shelf region. Further, in terms of percentage contributions made by the acetic acid leaches to the bulk samples it varies from 23-36%, 26-80% and 63-82% in the inner shelf, outer shelf and slope regions respectively. It is also observed that the distribution of phosphate in this fraction broadly follows that of phosphate content in the bulk samples.

In marked contrast to the above region in the Mangalore-Cochin sector, higher range of values of phosphate are encountered in the leaches of the inner shelf region, while in the outer shelf and slope regions, lower ranges of values of phosphate are encountered. But at the same time, in terms of percentage contributions made by this fraction to the concentrations in the bulk samples, they are higher in the inner (7.14 to 94.54%), outer shelf (10.5 to 100%) regions and lower in the slope region



(22.22 to 46.15%)—a trend opposite to the one observed in the Ratnagiri-Mangalore sector.

#### HCl leaches

Phosphate determinations in this fraction have been carried out in all three sectors and ranges of values of phosphate obtained and the ranges of percentage contributions made by this fraction to the concentrations in the bulk samples are given in Table I. From the data, it can be seen that in the shelf region between Indus Canyon and Port Dabhol, range of values obtained in the leaches of the inner shelf region are far lower than those obtained in the outer shelf region and the trend of values follow broadly the distribution of phosphate in the bulk sample, the range of variation in the inner shelf region is too wide and lower than that obtained in the outer shelf region where the range varies within 15% only. It must be mentioned here that since phosphate content in the acetic acid leaches has not been determined in the sediments of this region, the values obtained in the HCl soluble fraction include contributions made by the acetic acid leaches also (which represent that part of phosphate associated with carbonate phase, adsorbed and interstitial water phase). The higher values encountered in the outer shelf region could be due to this factor. In the Ratnagiri-Mangalore sector, in regard to the phosphate content in the leaches, on the minimum side they are the same for both inner shelf and outer shelf, while they are slightly higher in the slope region. In regard to the maximum values, they are on par in the inner shelf and slope regions while they are slightly lower in the outer shelf region. In terms of the percentage contributions made by this fraction to the concentrations in the bulk sample, they are lowest in the slope region, intermediate in the case of inner shelf and wider in the case of outer shelf. In the case of the shelf region between Mangalore and Cochin, the range of phosphate content encountered in the leaches of the inner shelf region are higher than the ranges met with in the outer shelf and slope regions. When these ranges are compared with the ranges for the corresponding zones in the shelf region between Ratnagiri and Mangalore, the ranges in the inner shelf are on par with those in the inner shelf in the northern region, while the ranges of the outer shelf and slope regions are far lower than those of the northern region. In terms of the percentage contributions made by this leach to phosphate content in the bulk samples, they vary from 0-69% in the inner shelf, 0-80% in the outer shelf and 0-61.5% in the slope region, indicating not much difference among the three zones.

#### HCl Insoluble Residues

In the Ratnagiri-Mangalore sector the contributions made by this fraction are uniformly low in all the three zones. They do not exceed 15% of the concentrations associated with the bulk samples. In the northern region (Indus Canyon to Port Dabhol) the contributions made by this fraction show a wide variation in the inner shelf region (40-75%) while in the outer shelf region they are very low and range between 15 and 30%. In the Mangalore-Cochin sector, over the entire region the contributions made by this fraction exhibit uniformly wide variations from almost 0 to as high as 87% in the inner shelf region and up to 75% in the outer shelf and slope regions.

## DISCUSSION

The distribution of phosphorus in the unconsolidated sediments is mainly controlled by (1) the phosphorus content of the mineral source material; (2) the concentration and state of dispersion of manganese and iron compounds in the sediment surface; (3) distribution of biogenous matter; and (4) chemical precipitation or replacement of existing solid phases. The effect of each of these factors on the distribution of phosphorus in these sediments is briefly discussed below separately.

### Mineral source material

The results presented in the preceding section have shown that phosphate in these sediments has both lithogenous and non-lithogenous component and the percentage contributions made by these components to the total concentrations of phosphate in the bulk samples vary widely from region to region. Heavy mineral studies carried out in these sediments have not indicated the presence of apatite. Monazite as a trace constituent is present in the sediments of the shelf region between Mangalore and Cochin and between Bombay and Daman (Mallik *et al.*, 1976; Siddiquie and Chowdhury, 1968; Kidwai *et al.*, 1981; Paropkari, 1983). Paropkari has not been able to find any direct correlation between the phosphate content and monazite content of the sediments. This perhaps could be due to the fact that a major part of phosphate content in these sediments is associated with other components. From the HCl soluble fraction it could be seen that a part of minerogenous contribution of phosphorus to the bulk concentration is obtained from the crystal lattice of the clay minerals.

### Manganese and iron compounds

The association of phosphorus with manganese and iron appear to result from the fact that the phosphorus, manganese and iron oxidates introduced into the oceans in dissolved and suspended form are largely deposited together in an oxidising environment. Further, the manganese and iron oxides precipitate phosphate from sea water in contact with sediment surface. Murty *et al.* (1973, 1980); Rao *et al.* (1976) have clearly established the presence of non-lithogenous iron and manganese in the form of hydroxides in the shelf sediments, particularly in higher concentrations in the inner shelf region. In view of this fact, and its negative correlation with manganese in the northern region and the lack of any correlation in the south, it seems possible that a part of phosphorus in these sediments was fixed in association with iron (as ferri-phosphate?).

### Distribution of biogenous matter

*Organic matter:* As already mentioned, the western continental shelf of India is subjected to upwelling with varying intensities from south to north and consequently, differences are found in the primary productivity from region to region. The distribution of organic matter over the entire continental margin shows that the sediments of the inner shelf and slope regions are characterised by higher organic carbon content and those of the outer shelf region by lesser content (Paropkari *et al.*, in press). Further, as between the organic carbon content of the inner shelf sediments and slope sediments, the latter have higher organic carbon content than those of the inner shelf sediments. The  $C_{org}/P_2O_5$  ratios (Table I)

from the different areas indicate the release of phosphorus from the decomposition of organic carbon in varying degrees. The correlation between organic carbon and phosphorus clearly indicates that a major portion of it is still bound with the organic carbon especially in the inner shelf and slope sediments.

*Calcareous material:* The distribution of phosphorous shows that higher content of phosphorus is associated with calcareous sediments especially between Gulf of Cambay and Mormugoa and in the slope region between Mormugoa and a little south of Karwar. Further south, phosphate content is low. The calcium carbonate present in these sediments is mostly contributed by oolites and shell fragments. These oolites and shell fragments are phosphatised to a certain extent as evidenced by the phosphate content in the acetic acid leaches of the sediments. Phosphatisation of the carbonate material is, however, not uniform, higher concentrations being associated with black-coloured oolites and shells and lower concentrations with the white or light-coloured ones. The absence of oolites and the presence of quartz sands in the outer shelf region of the southern region seem to be responsible for the low phosphate content in these sediments.

#### Chemical precipitation or replacement of existing solid phases

For the past four decades, discussions on the origin of marine phosphorites have been dominated by the hypothesis of Kazakov (1937) which relates the precipitation of phosphorite to upwelling of nutrient-rich waters. The mechanism which has been postulated is essentially simple and involves the supersaturation of sea water with respect to idealised 'apatite' as a result of the increase in pH and temperature which occurs when the relatively deep phosphate-rich water rises to the surface. Many elaborate schemes have been devised to account for the preferential precipitation of apatite rather than  $\text{CaCO}_3$  which is also assumed to precipitate under these conditions (Kolodny, 1981). Calculations of equilibrium solubilities with respect to idealised fluorapatite are not valid as the phosphatic mineral in phosphorites has very complex and far from adequately documented composition (McConnel, 1970). The other theory that marine phosphates originate from inorganic replacement of existing carbonate material is based on the fact that phosphate-rich solutions can convert calcite to carbonate apatite within a sediment (Ames, 1959). This process occurs by the partial replacement of  $\text{CO}_3^{2-}$  groups by  $\text{PO}_4^{3-}$  groups and may take place at the sediment water interface or at depth where phosphate is concentrated in interstitial waters.

Pytkowitz and Kester (1967) have concluded that the presence of phosphorites in sediments is due to geochemical or biochemical factors which controlled pH of the waters rather than high concentration of inorganic phosphorus. According to Baturin and Shishkina (1973), the interstitial environment in the anoxic sediments may offer a much more favourable site for phosphatisation. Baturin (1971), however, has emphasised that present day phosphorite is forming diagenetically and not by direct precipitation. Manheim *et al.* (1975) have concluded that four main requirements appear to control phosphorite enrichment: (1) strong and persistent upwelling system, (2) oxygen minimum zone impinging on the sea floor, (3) low influx of detrital mineral matter, and (4) limited supply of carbonate detritus. The formation of modern phosphorite under low dissolved oxygen and high dissolved phosphate have been indicated off the west coast of South America (Burnett *et al.*, 1980).

The inorganic phosphate content of the waters in the shelf region of India was found to be between 0.4 and  $3.0 \mu\text{M dm}^{-3}$  (Reddy and Sankaranarayanan, 1968; Sen Gupta and Naqvi, 1984). The concentrations of inorganic phosphate content of the interstitial waters of the sediments were found to be higher than the concentrations encountered in the overlying waters. They were found to range from 5000 to 7000  $\mu\text{g/litre}$  (unpublished data). The higher phosphate content in algal limestones as opposed to other types of limestones (Nair, 1985) and the distinct correlation that exists between organic carbon and phosphate content establishes a genetic relationship between organic carbon and phosphate in the sediments through diagenetic changes that are operative both at the mud water interface and within the sediments. A suitable substrate, i.e., calcareous sediments, is ideally suited for this purpose. The intensity of the process of phosphatisation may vary from site to site due to variations in the intensity of upwelling as evidenced by the frequency distribution pattern of *Globigerina bulloides* (Setty, 1983) and from wind stress studies (Shetye *et al.*, 1984) and hence the variations found in the phosphate content in the sediments of the shelf region, especially in the outer shelf. The low dissolved oxygen and high phosphate concentrations in the bottom waters could also result in some of the observed features, i.e., high phosphate content of the outer shelf and slope sediments.

In the continental slope region where organic carbon content is found to be very high and reducing conditions prevail, more and more phosphorus would go into solution and under favourable conditions get mineralised as apatite. Thus the presence of reducing muds beneath the oxygen minimum layer and denitrification (Sen Gupta and Naqvi, 1984) and perhaps also sulphate reduction resulting in the consumption of hydrogen ions in the slope region constitutes a favourable site for the precipitation of phosphate from the interstitial waters. X-ray diffractograms of a few sediments from the slope region off Kerala coast have revealed the presence of apatite peak in these samples. (Fig. 2.)

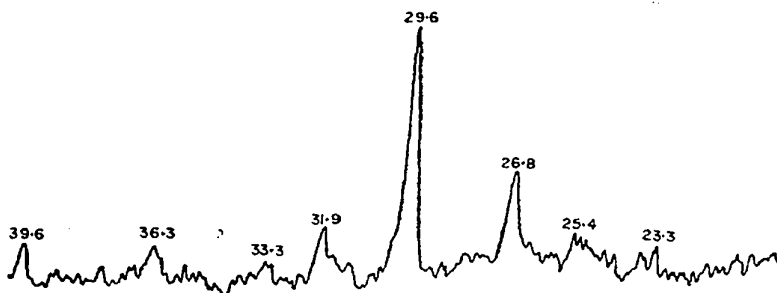


Figure 2. X-ray diffractogram of a sediment sample showing apatite peak ( $31.9^{\circ}2\theta$ )

Evidence of association of cold water foraminifera like *Globigerina bulloides* (Shetty, 1983), enrichment of organic matter and impoverishment of oxidate elements such as Mn (Rao, 1983; Paropkari, 1983) with phosphatic-rich sediments bespeaks of a highly productive environmental regime with limited detrital input and anoxic bottom conditions in the slope region. Such a regime corresponds well with the

concept of formation of phosphorite as a replacement of calcareous matter in an anoxic, organic-rich interstitial water milieu. Similar environment is also documented from S.W. African shelf and off Peru-Chile (Baturin, 1971; Baturin *et al.*, 1972; Veeh *et al.*, 1973; Manheim *et al.*, 1975).

From the present data it is difficult to differentiate between the two processes namely (1) precipitation from the interstitial waters (2) replacement  $\text{CO}_3^{2-}$  ion by  $\text{PO}_4^{3-}$ . It is quite possible that both precipitation and replacement processes are operative in this region but it is difficult to assess which dominated over the other.

In addition, in the mud bank regions of Kerala coast which are rich in organic carbon, X-ray analysis of the clay fractions have revealed the presence of apatite peaks (Nair and Murty, 1968). Neither the inner shelf region, where the organic rich sediments are present and are associated with recurring fish mortality nor the slope region could be ignored while prospecting for phosphorite deposits.

### Factor Analysis

Factor analysis was employed for two sets of data, i.e., one from Ratnagiri to Mangalore and the other from Mangalore to Cochin.

In the region between Ratnagiri and Mangalore, factor analysis has revealed three factors which are responsible for observed distribution of phosphorus in the sediments. Factor I is (fine-grained aluminosilicates and organics factor) characterised by subordinate loadings on P(T) and no loadings on P(NL), thus suggesting the effects of the element incorporation into crystal lattice structures and complexation with organics. Factor II (carbonate factor) has relatively high subordinate loadings on P(NL) which can be accounted for by the contribution of authigenic apatite to the carbonate factor. Factor III (organic carbon factor) which has high loadings on P(T) as well as P(NL) indicate the genetic relationship between organic matter and phosphorus.

In the second region, between Mangalore and Cochin, phosphorus has significant loadings on two factors i.e. Factor I (fine-grained aluminosilicate) and Factor II (carbonate factor). In the case of Factor I, the higher loadings on  $\text{P}_2\text{O}_5$  indicate the presence of phosphorus in fine-grained sediments as ferriphosphate, adsorbed phosphate, with some contribution from  $\text{C}_{\text{org}}$  which has, in turn, significant loadings on Factor I. On the contrary, the loadings on P in Factor II are very low suggesting that a very small fraction of phosphorus in these sediments is present as authigenic apatite. This is obvious as the region occupied by high carbonate sediments in this part of the shelf is very small (localised to few patches) and moreover the overall carbonate content of these sediments is also low. But at the same time, as mentioned earlier, peaks of apatite are observed in some of the X-ray diffractograms.

### CONCLUSIONS

1. These studies have established genetic relationship between phosphorus and organic carbon in a large part of the western continental margin of India.
2. In the inner shelf region phosphorus is also partly associated with iron (as ferri-phosphate?).
3. Variations of phosphorus content in the outer shelf and slope regions is attributed to the variation in the intensity of upwelling along the western continental margin of India as evidenced from the foraminiferal studies and wind stress distribution.

4. Environmentally, the western continental margin of India is very similar to other regions like Peru-Chile, S. W. Africa, where recent phosphatisation is reported.

5. The distribution of phosphorus suggests that the outer shelf/slope region between Bombay and Quilon and the mud bank regions of Kerala coast are promising areas for detailed exploration.

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#### References

- AMES, L. L., (1959) Genesis of carbonate apatite. *Econ. Geol.*, v. 54, pp. 829-841.
- BANSE, K., (1968) Hydrography of the Arabian Sea shelf of India and Pakistan and effects on dimersal fishes. *Deep-Sea Research*, v. 15, pp. 45-79.
- BATURIN, G. N., (1971) Formation of phosphate sediments and water dynamics. *Oceanology*, v. 11, pp. 373-376.
- BATURIN, G. N., MERKULOVA, K. I. and CHALOV, P. I., (1972) Radiometric evidence for recent formation of phosphatic nodules in marine shelf sediments. *Mar. Geol.*, v. 13, pp. 437-441.
- BATURIN, G. N. and SHISHKINA, O. V., (1973) Behaviour of fluorine during phosphorite formation in the ocean. *Oceanology*, v. 4, pp. 523-526.
- BATURIN, G. N., (1981) Phosphorites on the sea floor, origin, composition and distribution. Elsevier Scientific Publishing Company, New York, pp. 1-343.
- BENTOR, Y. K., (1980) Phosphorites—The unsolved problems. *In: Y. K. Bentor (Ed.). Marine Phosphorites SEPM Special Publication*, no. 29, pp. 3-18.
- BURNETT, W. C., VEEH, H. H. and SOUTAR, A., (1980) U-series, oceanographic and sedimentary evidence in support of recent formation of phosphate nodules off Peru. *In: Y. K. Bentor (Ed.). Marine Phosphorites, SEPM Special Publ. Tulsa, Oklahoma*, no. 29, pp. 61-71.
- BURNETT, W. C., ROE, K. K. and PIPER, D. Z., (1983) Upwelling and phosphorite formation in the ocean. *In: E. Suess and J. Thiede (Eds.). Coastal Upwelling and its sediment Record*, Plenum Press, New York, pp. 377-397.
- DIETZ, K. S., EMERY, K. O. and SHEPARD, F. P., (1942) Phosphorite deposits on the sea floor off Southern California. *Bull. Geol. Soc. America*, v. 53, pp. 815-847.
- EMERY, K. O. and DIETZ, R. S., (1950) Submarine phosphorite deposits off California and Mexico. *Cal. Jour. Mines and Geol.*, v. 46, pp. 7-15.
- KAZAKOV, A. V., (1937) The phosphorite facies and genesis of phosphorite. *In: Geol. Investigations of Agricultural Ores. Trans. Siest. Fertilizers and Insecto-Fungicides*, v. 142, pp. 95-113.
- KIDWAI, R. M., NAIR, R. R. and HASHIMI, N. H., (1981) Heavy minerals in the sediments on the outer continental shelf between Vengurla and Mangalore, West Coast of India. *Jour. Geol. Soc. India*, v. 22, pp. 32-38.
- KOLODNY, Y., (1981) Phosphorites: *In: C. Emiliani (Ed.). The Sea. Wiley-interscience*, New York, v. 7, pp. 981-1023.
- MADHUSUDANA RAO, CH., (1978) Distribution of  $\text{CaCO}_3$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in sediments of the northern half of western continental shelf of India. *Indian Jour. Mar. Sci.*, v. 7, pp. 151-154.
- MALLIK, T. K., VENKATESH, K. V., RAO, V. R. and RAMAMURTHY, M., (1976) Heavy mineral distribution patterns in the northern part of the Arabian Sea, western continental shelf of India. *Indian Jour. Earth Sci.*, v. 3, pp. 178-187.
- MANHEIM, F., ROWE, G. and JIPA, D., (1975) Marine phosphorite formation off Peru. *Jour. Sed. Petrol.*, v. 45, pp. 243-251.

- MARCHING, V., (1972) Zur Geochemie Rezentor Sedimente des Indischen Ozeans. 'Meteor', Forschungsergeb Reiche-6, v. 11, pp. 1-104.
- McCONNELL, D., (1973) Apatite: Its crystal chemistry, mineralogy, utilization and Biologic occurrences. Springer-Verlag, New York, pp. 111.
- McKELVEY, V. E., (1966) Successful new techniques in prospecting for phosphate deposits. *Aust. Min.*, v. 58, pp. 8-13.
- (1967) Phosphate Deposits. *U.S. Geol. Surv. Bull.*, v. 1252-D, pp. 1-21.
- MURRAY, J. and RENARD, A. F., (1891) Voyage of 'HMS Challenger' during the years 1873-1876. *Rep. on Deep Sea Deposits*, Chapt. 6, Part III, pp. 378-391.
- MURTY, P. S. N., REDDY, C. V. G. and VARADACHARI, V. V. R., (1968) Distribution of total phosphorus in the shelf sediments of the west coast of India. *Proc. Nat. Inst. Sci. India*, v. 34B, pp. 134-141.
- MURTY, P. S. N., RAO, CH. M. and REDDY, C. V. G., (1973) Partition pattern of iron, manganese, nickel and cobalt in the sediments off the west coast of India. *Indian Jour. Mar. Sci.*, v. 2, pp. 6-12.
- MURTY, P. S. N., RAO, CH. M. and PAROPKARI, A. L., (1980) Distribution patterns of aluminium, manganese, nickel, cobalt and copper in the non-lithogenous fraction of sediments of the northern half of the western continental shelf of India. *Indian Jour. Mar. Sci.*, v. 9, pp. 56-61.
- NAIR, R. R., (1969) Phosphatised oolites on the western continental shelf of India. *Proc. Natl. Inst. Sci. India*, v. 35A, pp. 858-863.
- (1985) Holocene phosphorites of the western continental margin of India. *Mahasagar, Bull. Inst. Oceanogr.*, v. 18, pp. 273-279.
- NAIR, R. R. and HASHIMI, N. H., (1980) Holocene climatic inferences from the sediments of the western Indian continental shelf. *Proc. Ind. Acad. Sci.*, (Earth and Planetary Science), v. 89, pp. 299-315.
- NAIR, R. R. and MURTY, P. S. N., (1968) Clay mineralogy of Mud Banks off Cochin. *Curr. Sci.*, v. 37, pp. 589-590.
- O'BRIEN, G. W. and VEEH, H. H., (1980) Holocene phosphorite on the east Australian Continental margin. *Nature*, v. 288, pp. 690-692.
- (1983) Are phosphorites reliable indicators of upwelling? *In: E. Sucs and J. Thiede* (Eds.), *Coastal upwelling and its sediment record*. Plenum Press, New York, pp. 399-419.
- PAROPKARI, A. L., (1983) Geochemical studies of the shelf and upper slope sediments off Mangalore-Cochin western continental margin of India. Ph.D. Thesis (Unpublished), IIT, Bombay, pp. 320.
- PYTKOWITZ, R. M. and KESTER, D. R., (1967) Relative calcium phosphate saturation in two regions of the North Pacific Ocean. *Limnol. Oceanogr.*, v. 12, pp. 714-718.
- QASIM, S. Z., (1977) Biological productivity of the Indian Ocean. *Indian Jour. Mar. Sci.*, v. 6, pp. 122-137.
- RAO, CH. M., MURTY, P. S. N., RAJAMANICKAM, G. V. and PAROPKARI, A. L., (1978) Distribution of phosphate in the sediments of the northern half of the western continental shelf of India. *Indian Jour. Mar. Sci.*, v. 7, pp. 146-150.
- RAO, CH. M., (1983) Geochemistry of the sediments of the central western continental shelf of India. Ph.D. Thesis (Unpublished), Andhra Univ., Waltair, 343 p.
- REDDY, C. V. G. and Sankaranarayanan, V. N., (1968) Distribution of nutrients in the shelf waters of the Arabian sea along the west coast of India. *Bull. Natn. Inst. Sci. India.*, v. 38, pp. 206-220.
- RILEY, J. P., (1958) Rapid analysis of silicate rocks and minerals. *Anal. Chem. Acta.*, v. 19, pp. 413-428.
- SEN GUPTA, R. and NAQVI, S. W. A., (1984) Chemical oceanography of the Indian Ocean, North of the Equator. *Deep-Sea Res.*, v. 31A, pp. 671-706.

- SETTY, M. G. A. P. and MADHUSUDANA RAO, CH., (1972) Phosphate, carbonate and organic matter distribution in sediment cores off Bombay, Saurashtra coast, India. 24th Internat. Geol. Congress, Canada, Section, 8, pp. 182-191.
- SETTY, M. G. A. P., (1983) Upwelling along the western Indian continental margin and its geological record: A summary. *In*: J. Thiede and E. Suess (Eds.). Coastal upwelling: Its sediment Record. Part B, sedimentary Records of Ancient Coastal Upwelling, Plenum Press, New York, pp. 201-213.
- SHARMA, G. S., (1966) Thermocline as an indicator of upwelling. *Jour. Mar. Biol. Assn. India*, v. 8, pp. 8-19.
- SHETYE, S. R., SHENOI, S. S. C., ANTONY, M. K. and KRISHNAKUMAR, V., (1985) Monthly mean wind stress along the coast of the north Indian Ocean. *Proc. Indian Acad. Sci.*, v. 94, pp. 129-137.
- SIDDIQUIE, H. N. and CHOWDHURY, A. N., (1968) The distribution of phosphate in some samples of the shelf sediments off the west coast of India. *Bull. Natn. Inst. Sci. India*, v. 38, pp. 483-490.
- SIDDIQUIE, H. N., GUJAR, A. R., HASHIMI, N. H. and VALSANGKAR, A. B., (1984) Superficial mineral resources of the Indian Ocean. *Deep-Sea Res.*, part A, v. 31, nos. 6-8A, pp. 763-812.
- STACKELBERG, U. V., (1972) Facies of sediments of the Indian Pakistan continental margin (Arabian Sea). 'Meteor' Forsch-Ergebnisse, Berlin-Stuttgart, Reihe-C, no. 9, pp. 1-136.
- TOOMS, J. S. and SUMMERHAYES, C. P., (1968) Phosphatic rocks from the northwest African continental shelf. *Nature*, v. 218, pp. 1241-1242.
- TOOMS, J. S., SUMMERHAYES, C. P. and CRONAN, D. S., (1969) Geochemistry of marine phosphate and manganese deposits. *Ann. Rev. Oceanogr. Mar. Biol.*, v. 7, pp. 49-100.
- VEEH, H. H., BURNETT, W. C. and SOUTER, A., (1973) Contemporary phosphorites on the continental margin of Peru. *Science*, v. 181, pp. 844-845.
- VON DER BORCH, C. C., (1970) Phosphatic concretions and nodules from the upper continental slope, northern New South Wales. *Geol. Soc. Austr. Jour.*, v. 16, pp. 755-759.
- WATTERS, W. A., (1968) Phosphorite and apatite occurrences and possible reserves in New Zealand and outlying islands. *N. Z. Geol. Surv. Rep.*, v. 33, p. 15.