

## Distribution of Phosphate in Sediments of the Northern Half of the Western Continental Shelf of India

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The study has revealed that (i)  $P_2O_5$  content in the sediments varies from 0.17 to 1.2%, (ii) fine grained sediments of terrigenous origin occupying innershelf region between Gulf of Cambay and Port Dabol and greater part of the shelf region north of Gulf of Cambay up to Indus Canyon contain low percentages of phosphate (< 0.2 to 0.3%), typical for normal marine sediments, while the relict zone of the outershelf region between Gulf of Cambay and a little south of Bombay and the upper Continental slope region contain relatively high content of  $P_2O_5$ , and (iii)  $P_2O_5$  content of the acid soluble fractions of the sediments also exhibits a similar trend. These distribution patterns are discussed in relation to the distribution patterns of the sediments and their chemistry and the hydrographic features of the overlying waters. From these studies, it is 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.

**D**EPOSITS of several types of minerals, including phosphorite, on the continental shelves of the world are characteristic of the environment in which they are found. The occurrence of phosphorite deposits has been reported off the coasts of several countries<sup>1-7</sup>. These deposits have long 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<sup>8-11</sup>. Although some of the phosphate deposits are undoubtedly detrital, most of them are considered to be hydrogenous in nature and have been related to pronounced upwelling observed in the areas where they are found<sup>8,9</sup>. Since the western continental shelf of India is also subjected to seasonal upwelling<sup>12-14</sup> a detailed study of the distribution pattern of phosphate has been taken up with a view to delineating areas of enrichment, if any, for detailed exploration. As a part of this programme, distribution pattern of phosphate has been studied in the sediments of the northern half of the western continental shelf of India and the results obtained are presented in this paper. Although there are a few earlier accounts on this subject<sup>15-18</sup> it may be mentioned that they did not throw much light as they are based on the study of samples which are few and far between.

### Materials and Methods

The study area from which the sea floor sediment samples were collected covers the northwestern continental shelf of India extending from Indus Canyon in the north to Ratnagiri<sup>19</sup> in the south. In all about 90 stations were occupied for sampling and they were distributed along 14 sections normal to the coast. All samples were collected using a La-Fond-Dietz snapper. Along most of the sec-

tions, samples were collected between 20 and 100 m water depth on the coastal and seaward sides respectively while along a few sections sampling on the seaward side was extended up to 150 to 250 m depth. Dissolved oxygen and water column phosphate analyses were performed aboard the ship<sup>20</sup>. Biological investigations such as primary productivity and zooplankton were also made wherever possible.

Representative samples were obtained from the collections made at each station and a suitable amount of each sample was digested with hydrofluoric and perchloric acids following the method of Chester and Hughes<sup>21</sup> for the determination of phosphate in the bulk samples. Further, in order to understand the extent to which the phosphate is associated with the acid soluble fractions of the sediments, they were leached with 3N HCl and the phosphate concentrations in the bulk samples as well as in the acid soluble leaches were determined colorimetrically following the method of Riley<sup>22</sup>. In addition, a few of the limestones dredged from the outershelf region during the cruises of *RV Gaveshani* and oolites and shells separated from a few samples collected from the outershelf region were also utilized in the present study.

### Results and Discussion

In the region under study, the continental shelf is characterized by certain well defined features in regard to the distribution pattern of sediments and their chemistry. In general, texturally, fine-grained sediments of terrigenous origin occupy a greater part of the continental shelf between Indus Canyon and Gulf of Cambay while further southward their deposition is confined up to 60-65 m, beyond which, the shelf is characterized by the presence of coarse grained sediments (sands, silty or clayey

sands, etc.). These coarse grained sediments are relict in nature and are marked by a high calcium carbonate content<sup>23</sup>. The distribution patterns of calcium carbonate and the percentages of acid insolubles<sup>24</sup> indicate that the outershelf region between Gulf of Cambay and Port Dabol is relatively free from accumulation of terrigenous material. Organic carbon ranges from about 0.25 to 2.5% in these sediments. With a few exceptions, while >1% of organic carbon is usually associated with the fine grained sediments of the innershelf region, <1% is associated with the coarse grained sediments of the outershelf region.

The distribution patterns of phosphate in the bulk samples as well as in the acid soluble fractions of the sediments are shown in Figs. 1 and 2. A careful examination of these figures along with the texture and distribution patterns of the sediments and the analyses of the dredged limestones, oolites and shells have enabled the following inferences to be drawn in regard to the distribution patterns of phosphate:

(1) In the unconsolidated sediments, on the bulk sample basis the phosphate content ranges from 0.17 to 1.2%.

(2) With the exception of the high values of 0.8 to 1% of phosphate associated with the finegrained sediments of the innershelf region between River Savitri and Port Dabol, lower ranges of phosphate (<0.2% and 0.2 to 0.3%) are generally associated with the finegrained sediments of terrigenous origin in the rest of the shelf region.

(3) In the shelf region between Gulf of Cambay and Bombay, the phosphate content in the sediments exhibits an increasing trend away from the coast with higher ranges of phosphate (0.3 to 0.4%; 0.4 to 0.5% and >1%) associated with the relict carbonate sediments of the outershelf region.

(4) The black coloured oolites and shells and portions of the dredged limestones have phosphate content ranging from 0.8 to 1.2% while the grey coloured oolites and shells and limestones have only 0.1 to 0.2% of phosphate.

(5) The phosphate content in the acid soluble leaches of the unconsolidated sediments ranges from 0.12 to 0.99%. Distribution pattern of phosphate in this fraction is broadly similar to that obtained in the bulk samples. Further, calculations made on the per cent contributions made by the acid soluble fraction to the concentrations in the bulk samples have revealed that they are far less in the finegrained sediments of the inner shelf region as compared to those in the relict sediments of the outershelf region which is indicative of the authigenic nature of phosphate associated with relict sediments to a great extent.

Deposits of phosphatic nodules, pellets and phosphate rock are confined mainly to nearshore areas in depths of water not exceeding 1000 m. Modern phosphatic assemblages can occur in at least 2 kinds of association: (i) in areas of high organic productivity associated with reducing conditions during their formation and (ii) in areas which do not have a high organic productivity and associated with oxidizing conditions in the environment<sup>25</sup>.

Although as indicated earlier, some of the phosphate deposits are undoubtedly detrital, others are hydrogenous and several theories have been put forward to explain the existence of the latter deposits. The 2 most probable ones are: (i) that they are primary chemical precipitates and (ii) that they are an incomplete replacement product formed from preexisting carbonate material. According to the chemical precipitation theory advanced by Kazakov<sup>26</sup> and accepted subsequently by several others, phosphorus in the uppermost 100 m of ocean waters is taken up by phytoplankton and is returned to solution as orthophosphate ions on death of the organisms, when they sink down the water column. Since sea water is undersaturated with respect to apatite, any phosphorus which is brought down by the organisms does not precipitate from solution on hydrolysis of the organic matter and in areas of upwelling it is returned to the upper water layers. This upwelling of phosphate-rich deep water is accompanied by a decrease in the partial pressure of CO<sub>2</sub> and an increase in pH in the surface layers where the phosphate promotes a high productivity. As a result, phosphate saturation can be reached in some shallow latitude areas where increased pH of the water can result in the precipitation of phosphate minerals. In addition to the upwelling of phosphate rich deeper water masses, Kramer<sup>27</sup> has suggested that river run-off of continental water which has flowed over carbonate rocks and so has a high pH, may cause the precipitation of marine phosphates. The second theory that marine phosphates originate from the inorganic replacement of existing carbonate material is based on the fact that phosphate-rich solutions can convert calcite to carbonate-apatite within a sediment<sup>11</sup>. This process occurs by the partial replacement of CO<sub>3</sub> groups by PO<sub>4</sub> groups and may take place at the sediment-water interface, or at depth within a sediment when phosphate is concentrated in interstitial waters. This replacement mode has been documented by Ames<sup>28</sup> in laboratory experiments.

Pytzkowitz and Kester<sup>29</sup> have concluded that the presence of phosphorites in the sediments is due to the geochemical or biochemical factors which controlled pH of the waters rather than to high concentration of inorganic phosphorus. According to Baturin and Shishkina<sup>30</sup> the interstitial environment in the anoxic sediments may offer a much more favourable site for phosphatization. Manheim *et al.*<sup>31</sup> who worked on the marine phosphorite formation off Peru have concluded that 4 main requirements appear to control phosphorite enrichment: (i) there must be an exceptionally strong and persistent upwelling system capable of providing both a continuing and large supply of organic detritus, (ii) an oxygen minimum zone impinging on the sea floor that permits maintenance of an organic-rich substrate and high concentration of dissolved phosphate in the interstitial water; phosphate rich water above the sediment-water interface is required to support surface productivity, (iii) supply of detrital mineral matter must be low such that phosphorite is not diluted excessively and (iv) there must be a limited supply of carbonate detritus. Rather than

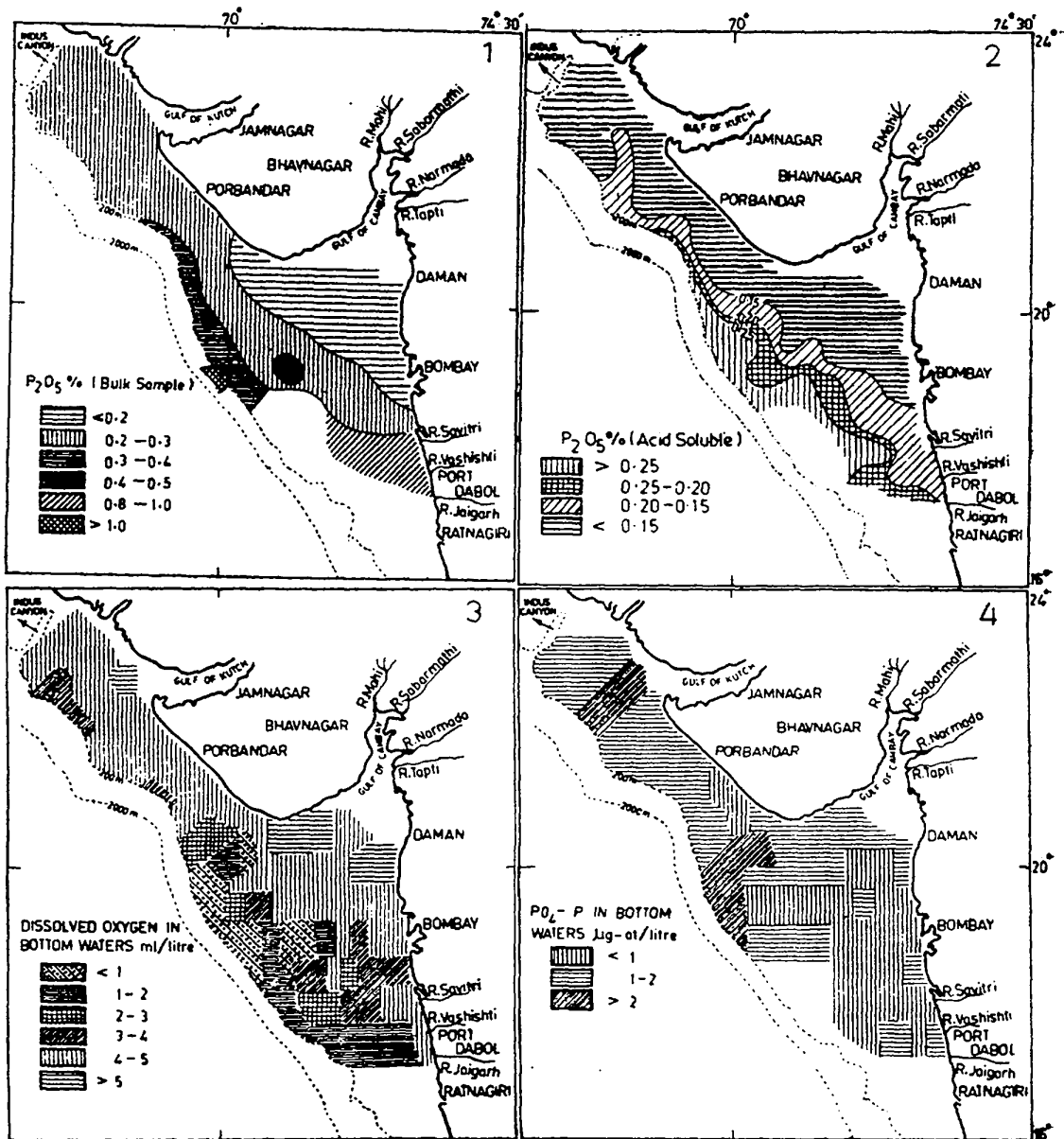


Fig. 1 — Phosphate distribution in the bulk samples

Fig. 2 — Phosphate distribution in the acid soluble fractions of the sediment

Fig. 3 — Distribution of dissolved oxygen in the bottom waters

Fig. 4 — Distribution of  $PO_4$ -P in the bottom waters

being supplied continuously, benthic foraminifera may proliferate intermittently due to variations in the upwelling and the intensity and death of oxygen minimum, so that the small carbonate tests would be phosphatized on resumption of normal organic accumulations and anoxic conditions.

The presence of strong seasonal upwelling along the western continental shelf of India between Bombay and Quilon is well documented<sup>12-14</sup>. These studies have revealed that there is a time lag in the occurrence of this phenomenon from south to north followed by a decrease in its intensity also from

south to north. Although information on the upwelling process in the shelf region north of Bombay up to Indus region is not available, considering the various meteorological and oceanographic parameters, the presence of upwelling along this part of the shelf cannot be precluded.

Distribution patterns of dissolved oxygen and inorganic phosphate ( $\text{PO}_4\text{-P}$ ) measured in the bottom waters at the time of the collection of the sediment samples (Dec. 73-May 74) are shown in Figs. 3 and 4. Except for a small portion in the outershelf region between Gulf of Cambay and a little south of Bombay, the shelf region is covered by oxygenated waters only.  $\text{PO}_4\text{-P}$  distribution (Fig. 4) shows that the waters north of Gulf of Cambay are characterized by comparatively higher concentrations of  $\text{PO}_4\text{-P}$  than the waters to the south of Gulf of Cambay and concentrations exceeding 2 mg at/litre are encountered only in 2 regions, viz. off Gulf of Kutch and in the outershelf region off Gulf of Cambay and Bombay. In the continental slope region, there exists an oxygen minimum layer with increasing concentrations of  $\text{PO}_4\text{-P}$ . Underlying this oxygen minimum layer are the grey and olive green muds rich in organic carbon. Computations made on the trivalent phosphate ion concentrations in the waters (in which form phosphate is incorporated in the sediments) along a few sections have revealed that (i) its concentration varies from  $1.16 \times 10^{-7}$  to  $6.67 \times 10^{-7}$  g mols/litre, (ii) its concentrations show a decreasing trend away from the coast along any given section and (iii) relatively the concentrations associated with the waters north of Bombay are slightly higher than those associated with the waters south of Bombay. According to Naik<sup>32</sup>, the shelf waters are by and large saturated with tricalcium phosphate and no precipitation in the water column may be due to the several inhibiting factors as mentioned by McConnel<sup>33</sup>. Estimations of  $\text{PO}_4\text{-P}$  in the interstitial waters of the core samples collected along one section between Bombay Harbour and Bombay High Region have revealed that their concentrations range from 2.28 to 73.31 mg at/litre in the surficial sediments while in the bottom portions of the core samples they range from 4.56 to 59.84 mg at/litre<sup>34</sup>. An examination of these concentrations in relation to the texture of the sediments and the organic matter content has revealed that higher concentrations are associated with finegrained sediments rich in organic matter while lower concentrations are associated with coarse sediments poor in organic matter.

Primary productivity measurements carried out using <sup>14</sup>C technique have revealed the following range of values for the regions north and south of Gulf of Cambay<sup>35</sup>: (i) Indus river discharge coastal area and Saurashtra coast — 0-50 m: 1 gC/m<sup>2</sup>/day and 50-200 m: 0.5-1 gC/m<sup>2</sup>/day and (ii) south of Gulf of Cambay (av. for shelf): 0.5-1 gC/m<sup>2</sup>/day. These results go to show that in general, while the entire shelf region under study is characterized by a high rate of productivity, the region north of Gulf of Cambay has a higher rate of production than the region south of it. Zooplankton biomass distribution studies have revealed that higher intensity of zooplankton cells was from the region

between 20-23°N and 66-70°E and the north-eastern part of the Arabian Sea is far richer than any other region in the Arabian Sea in its biomass content<sup>36</sup>.

Phosphate content in the sediments exhibits a distinct distribution pattern both on the bulk sample basis as well as in the acid soluble fractions of the sediments. The fine grained sediments of the innershelf region between Gulf of Cambay and River Savitri and the greater part of the shelf sediments north of Gulf of Cambay up to Indus Canyon are characterized by low values of  $\text{P}_2\text{O}_5$  typical for normal marine sediments, while the coarse grained sediments of relict nature of the outer shelf region between Gulf of Cambay and little south of Bombay have phosphate content ranging from 0.3 to 1.2%. A similar trend is also observed for the phosphate content of the acid soluble fractions. In spite of the generally high productivity of the overlying waters and the relatively high trivalent phosphate ion concentrations in the coastal waters as compared to the outershelf region, the low values associated with the fine grained sediments could be due to (1) rapid sedimentation of the fine grained inorganic detritus of terrigenous origin taking place in the region and (2) high dissolved oxygen content of the waters which may be responsible for the oxidation of the organic material in the water column itself. The low organic carbon content (1-2%) of the underlying sediments supports this conclusion. As against this situation the outer shelf region between Gulf of Cambay and little south of Bombay is comparatively free from accumulation of terrigenous material and in spite of the poor organic carbon content of the sediments relatively high  $\text{P}_2\text{O}_5$  content associated with these sediments and their associated oolites, shells and limestones appear to be due to some favourable biochemical/geochemical factors for the partial replacement of carbonate group by the trivalent phosphate group. One sample collected from 270 m depth from the upper continental slope (off Bombay) has a  $\text{P}_2\text{O}_5$  content of 1.2% on the bulk sample basis and 0.99% in the acid soluble fraction. Environmentally the sample comes from the oxygen minimum zone present in the slope region and is characterized by a high organic carbon content 2.42% and relatively low calcium carbonate content as compared to the adjacent outershelf region. From the broad similarity observed in the environmental conditions between the slope region off Peru coast and the north-western continental slope of India, the possibility of intense phosphatization of the calcareous material cannot be precluded. Therefore, it is tentatively suggested that the outer continental shelf region between Gulf of Cambay and little south of Bombay and the Continental slope region in the area of study are environmentally favourable for detailed exploratory studies for phosphates.

High phosphate content (0.8 to 1.0%) on the bulk sample basis associated with the fine grained sediments of the innershelf region between River Savitri and Port Dabol and correspondingly very low phosphate content observed in the acid soluble fraction of the sediments suggest that the major portion of the phosphate content is of terrigenous origin. The presence of a number of small rivers

in this region and the apatite bearing rocks present in the hinterland lend support to this inference.

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