

Phosphate, Carbonate and Organic Matter Distribution in Sediment Cores Off Bombay-Saurashtra Coast, India

M. G. ANANTHA PADMANABHA SETTY and
C. MADHUSUDANA RAO,
India

ABSTRACT

Phosphate, organic matter and calcium carbonate content in five sediment cores (three from the outer shelf one from the slope and one from the basin) from the Arabian Sea have been determined. The distribution pattern indicates their close genetic relationship.

The total phosphorus value is high in the core from the slope, almost uniform in the cores from the outer shelf and a core from the nearby basin, but poor in a core (no. 3) considered to be from a 'closed basin' within the shelf. The total phosphorus is maximum (2140-1120 $\mu\text{g/gm}$ or 1.04-0.84% P_2O_5 on a carbonate-free basis) in the upper 7.5 cm of the slope sediment and minimum (105-80 $\mu\text{g/gm}$ or 0.025-0.022% P_2O_5) in similar sediment on the shelf. It is also higher in the oolitic fractions of the cores. The organic carbon closely fluctuates with increase and decrease of the phosphate content and ranges from 4.655% with 1.04% P_2O_5 in the top part of the core from the slope and 0.385% with 0.160% P_2O_5 in the bottom part of the core from the shelf. Calcium carbonate percentage is uniform in the sediments from the slope and basin region, but varies considerably in the cores from the shelf. It is typically very poor in core no. 3. Calcareous oolites are present in all the cores with the exception of one (no. 3). Further, it is proved that wherever phosphate is high, organic matter is also high because both are directly related to upwelling, luxuriant organic productivity, a non-depositional environment and the presence of abundant carbonate. It is suggested that the shelf slope region and the adjoining basin in the Bombay-Saurashtra coastal area represents one of the localities where modern phosphorite deposits are being formed.

INTRODUCTION

Five sediment cores from the Arabian Sea were obtained by the R/V *Oceanographer*, U. S. Coast and Geodetic Survey, during June 13-23, 1967. These were splits and have been shared by the senior author and the U. S. Environmental Science Service Administration. A description of the stratigraphy and lithology of the cores has been presented separately (Setty, 1972). The present paper is an account of the distribution of phosphate, carbonate and organic matter in these sediment cores: three cores (Nos. 3, 4 and 5, taken at stations 66, 73 and 146 at 19°32.8'N, 71°21.5'E, 20°10.0'N, 70°26.9'E and

Authors' addresses are given at the back of this book.

20°04.5'N, 69°26.0'E and at depths of 64, 73 and 63 m respectively) from the shelf; one (No. 1, taken at station 29, at 17°57.9'N 70°46.0'E and at a depth of 649 m) from the slope; and one (No. 2, taken at station 43 at 18°35.2'N, 69°17.2'E, and at a depth of 2,960 m) from the basin part of the Arabian Sea.

A total of 45 samples, taken from approx. 10-30 cm depth intervals from the 15 segments of the five cores, were analysed. This report presents the results of the analyses and the possible relationships that exist between the three constituents. They indicate one of the localities where modern phosphorite is being formed.

METHODS

Total calcium carbonate present in the sediment was determined using the Rapid Volumetric Analysis as described by Herrin *et al.* (1958), and total phosphorus by the method described by Rochford (1951). Estimations for phosphorus were made using the "Unicam" spectrophotometer and determining absorption at 700 m μ . The total phosphorus estimated here includes different forms of phosphorus, such as interstitial phosphate, adsorbed phosphate, organic phosphate and also insoluble inorganic phosphate. The organic carbon was determined by the El Wakeel and Riley (1957) method wherein the organic matter present in a sample is oxidised with a known quantity of chromic acid and titrated against ferrous ammonium sulphate. The value thus obtained is multiplied by a factor of 1.724 (as recommended by soil chemists), which represents the amount of organic matter present in the sample. Organic content generally is determined in terms of carbon or nitrogen present. Here it is determined in terms of carbon, as it is the most reliable index and also has a fairly constant relationship to nitrogen.

LITHOLOGY OF THE CORES

Of the three cores from the shelf (core Nos. 3, 4 and 5), No. 3 is from a 'closed basin' or trough within the shelf wherein the lithology consists of a very fine grained sapropelitic, dark greyish brown clayey material. It includes a high degree of carbonaceous matter, but is poor in foraminifera, pteropods, ostracods, embryonic molluscs, fish scales and teeth. No. 4 is from a region with an oolitic layer and has intercalations of soft, fine grained calcareous clayey material, is very poor in foraminifera, pteropods, whole and fragmental molluscs and includes fragments of bryozoa, fish teeth and spines of echinoderms. No. 5 is characterized by two distinct lithologies (a calcareous oolitic layer containing lenses of clastic material overlain by a sapropelitic layer), a definite stratigraphic break and a moderately rich fauna. No. 1 from the slope, is composed of a soft, light grey, calcareous clayey material with oolites which includes authigenic sediment and also slumped outer shelf oolitic material. The fauna include foraminifera, pteropods, oolites, fish scales and teeth, and juvenile adult and fragmental bivalves and gastropods. No. 2, from the Arabian basin consists of limy marl, Globigerina ooze, other biogenic material, fine-grained oolites and turbidite flows (Setty, 1972).

CARBONATES

Table 1 presents the percentage and distribution of calcium carbonate at various depths in the sediment samples of all the cores. They show a difference in percentage content from the shelf, through the slope to the basin. The variation in the three cores taken from the three different regions of the shelf between Bombay and the Saurashtra coast indicate the differences in the environmental conditions of deposition.

TABLE 1 — Percentage Distribution of Total Phosphorus, Organic Matter and Calcium Carbonate in 1-5 Sediment Cores at Different Depths

| SL. No. | Depth in CMS. | Total Phosphorus ($\mu\text{g/gm}$ Dry Weight) | P ₂ O ₅ (Per Cent, Carbonate-Free Basis) | Organic Carbon (Per Cent Dry Weight) | Organic Matter (Organic Carbon \times 1.724 Per Cent Dry Weight) | CaCO ₃ (Per Cent Dry Weight) |
|---------------------------|---------------|---|--|--------------------------------------|--|---|
| CORE No. 1 — SLOPE | | | | | | |
| 1 | 2 | 2140 | 1.04 | 4.655 | 8.00 | 51.7 |
| 2 | 25 | 1380 | 0.90 | 3.885 | 6.70 | 63.0 |
| 3 | 50 | 1120 | .84 | 2.345 | 4.00 | 68.7 |
| 4 | 60 | 1120 | .80 | 2.240 | 3.80 | 66.9 |
| 5 | 85 | 860 | .63 | 2.100 | 3.60 | 67.7 |
| 6 | 110 | 620 | .40 | 1.540 | 2.65 | 63.8 |
| 7 | 120 | 740 | .50 | 1.575 | 2.70 | 66.5 |
| 8 | 145 | 520 | .33 | 1.680 | 2.90 | 63.8 |
| 9 | 175 | 520 | .33 | 1.575 | 2.70 | 63.8 |
| CORE No. 2 — BASIN | | | | | | |
| 10 | 2 | 520 | 0.24 | 0.700 | 1.20 | 46.1 |
| 11 | 25 | 640 | .44 | 1.190 | 2.00 | 65.4 |
| 12 | 40 | 700 | .44 | 0.910 | 1.56 | 63.8 |
| 13 | 50 | 600 | .35 | .805 | 1.37 | 60.0 |
| 14 | 70 | 500 | .24 | .500 | 0.86 | 52.6 |
| 15 | 90 | 600 | .26 | 1.190 | 2.00 | 45.6 |
| 16 | 100 | 700 | .30 | 0.455 | 0.77 | 48.4 |
| 17 | 120 | 260 | .12 | 0.700 | 1.20 | 46.6 |
| 18 | 140 | 500 | .30 | 1.050 | 1.80 | 63.0 |
| 19 | 150 | 500 | .26 | 1.505 | 2.58 | 56.8 |
| 20 | 170 | 360 | .27 | 1.190 | 2.00 | 69.0 |
| 21 | 190 | 570 | .37 | 1.680 | 2.90 | 65.2 |
| CORE No. 3 — SHELF | | | | | | |
| 22 | 2 | 105 | 0.025 | 1.47 | 2.52 | 9.0 |
| 23 | 15 | 105 | .026 | 1.05 | 1.80 | 10.6 |
| 24 | 30 | 80 | .022 | 0.91 | 1.56 | 11.6 |

| SL. No. | Depth in CMS. | Total Phosphorus ($\mu\text{g}/\text{gm}$ Dry Weight) | P_2O_5 (Per Cent, Carbonate- Free Basis) | Organic Carbon (Per Cent Dry Weight) | Organic Matter (Organic Carbon \times 1.724 Per Cent Dry Weight) | CaCO_3 (Per Cent Dry Weight) |
|--------------------|------------------|---|---|---|---|---|
| 25 | 40 | 210 | .051 | 1.295 | 2.20 | 11.2 |
| 26 | 55 | 115 | .028 | 1.33 | 2.28 | 10.9 |
| 27 | 70 | 200 | .050 | 1.12 | 1.90 | 12.0 |
| 28 | 80 | 190 | .050 | 1.26 | 2.16 | 10.6 |
| 29 | 100 | 280 | .073 | 1.54 | 2.65 | 13.0 |
| 30 | 115 | 200 | .052 | 1.225 | 2.10 | 11.6 |
| CORE No. 4 — SHELF | | | | | | |
| 31 | 2 | 720 | 0.25 | 0.630 | 1.10 | 34.0 |
| 32 | 25 | 420 | .14 | .525 | 0.90 | 30.0 |
| 33 | 50 | 420 | .16 | .385 | .70 | 40.0 |
| CORE No. 5 — SHELF | | | | | | |
| 34 | 2 | 210 | 0.06 | 1.050 | 1.80 | 21.6 |
| 35 | 30 | 280 | .10 | 0.910 | 1.56 | 37.0 |
| 36 | 60 | 570 | .26 | 0.630 | 1.10 | 50.0 |
| 37 | 70 | 615 | .32 | .910 | 1.56 | 56.4 |
| 38 | 95 | 500 | .24 | .665 | 1.20 | 55.4 |
| 39 | 115 | 540 | .30 | 1.015 | 1.73 | 58.0 |
| 40 | 125 | 570 | .30 | 0.945 | 1.63 | 56.0 |
| 41 | 150 | 540 | .30 | .910 | 1.56 | 58.0 |
| 42 | 175 | 500 | .26 | .875 | 1.51 | 57.0 |
| 43 | 195 | 570 | .26 | .945 | 1.63 | 50.3 |
| 44 | 210 | 580 | .30 | .963 | 1.65 | 55.6 |
| 45 | 235 | 560 | .30 | 1.015 | 1.73 | 56.0 |

Among the three shelf cores, the calcium carbonate content in the top (sediment-water interface) layers varies from 9.0 to 34.0 to 21.6%. These values are related to the prevailing conditions of overlying water masses and the physico-chemical parameters. Very low values (9.0% in No. 3) represent reducing conditions, whereas the high values (34.0 and 21.6% in Nos. 4 and 5) indicate oxidising conditions. All three cores show, with a few fluctuations, an increase rather progressively downward to the base where values are 11.6, 40.0 and 56.0% respectively. These and the intermediate variables represent the actual composition of the lithology at those depths. Therefore, the changes in the abundance with depth, or with time, reflect the environment and other factors, such as changes in the type of original fauna and flora, rate of deposition, pH, Eh,

temperature, salinity, nutrients, saturation/supersaturation of other dissolved salts, organic productivity, upwelling and inflow into the region. Hulsemann (1968) suggests similar reasons for the changes noticed in the shelf sediment cores from the Florida-Hatteras region (JOIDES program). The data (Table 1) suggest that some of the notable intermediate variables at core depth are due to sudden changes in the sedimentary environment resulting immediately after (1) the influx of terrigenous material, consisting of fresh-looking quartz, feldspar and dark minerals, and possibly Ca^{++} ions, presumably leading to oxidising conditions favourable for high carbonate values (as seen in samples Nos. 14 and 20 in core No. 2, and Nos. 27 and 29 in core No. 3); and (2) some other influence, creating a definite stratigraphic break (as seen in sample No. 36, in core No. 5) which is reflected in low values. However, this last may also be due to the influence of the insoluble residue and the clay content in the lower part of the section (Fugel, 1968). Oolites and clayey material present in all the cores (with the exception of No. 3) are responsible for the surplus or deficit values of carbonate regardless of the contribution of calcareous biogenic sediment.

ORGANIC MATTER

Percentage distribution of both organic matter and organic carbon is shown in Table 1, which indicates that cores Nos. 1 and 3 are very rich in organic matter; it is present in moderate amounts in No. 2 and in 5, but is minimal in No. 4.

The top layers of all the cores are also rich in organic matter; it is very rich principally in No. 1 (8.00%), moderately high in Nos. 3 and 5 (2.52 and 1.80%), but poor in Nos. 2 and 4 (1.20 and 1.10%). It is lowest in the bottom of the layer in No. 4 (0.70%). Thus, all the cores, although generally showing high (though differing) values in the top layers, tend to decline in organic matter percentage with depth. Caspian Sea sediments show a similar relationship.

Normally, microorganisms, bacteria and burrowing animals are very active in the upper meter or so of the very recent sediments and are responsible for degrading some compounds and synthesizing others in addition to mixing sediments (samples Nos. 34, 35 and 36 in core No. 5; Setty, 1972); the rate of accumulation of organic matter is high. This accounts for the higher values in the upper part of the core from the slope and cores Nos. 3 and 5 on the shelf (Trask, 1939).

Table 1 shows very high values for organic carbon in core No. 1, where it decreases progressively with depth (from 4.655% at 2 cm. depth to 1.575% at 175 cm depth). This may be attributed to compaction, degradation, decomposition, loss of moisture and synthesis to other compounds during its diagenesis. The average organic carbon here is 2.0%. No. 2 differs from the above in exhibiting a few higher values (samples 11, 15, 19, 20 and 21) and lower values (13, 16 and 17) at certain lower sections. This may be due to the influence of turbidity flows from the adjoining shelf/slope which introduced organic matter. The content then declined when the typical basin sedimentation reverted to normal (Setty, 1972). The average organic carbon here is 0.99%. No. 3 shows higher values with depth (1.470 to 1.255% at 115 cm). Here, the grain size of the clayey material, in the prevailing reducing environment, retains the organic carbon and prevents its decomposition. The average organic carbon here is 1.244%. No. 4 has low values; however, even they decrease with depth (0.630 to 0.385% at 50 cm). This may be due to the coarse-grained nature of the sediment and the influence of the influx of clastic material.

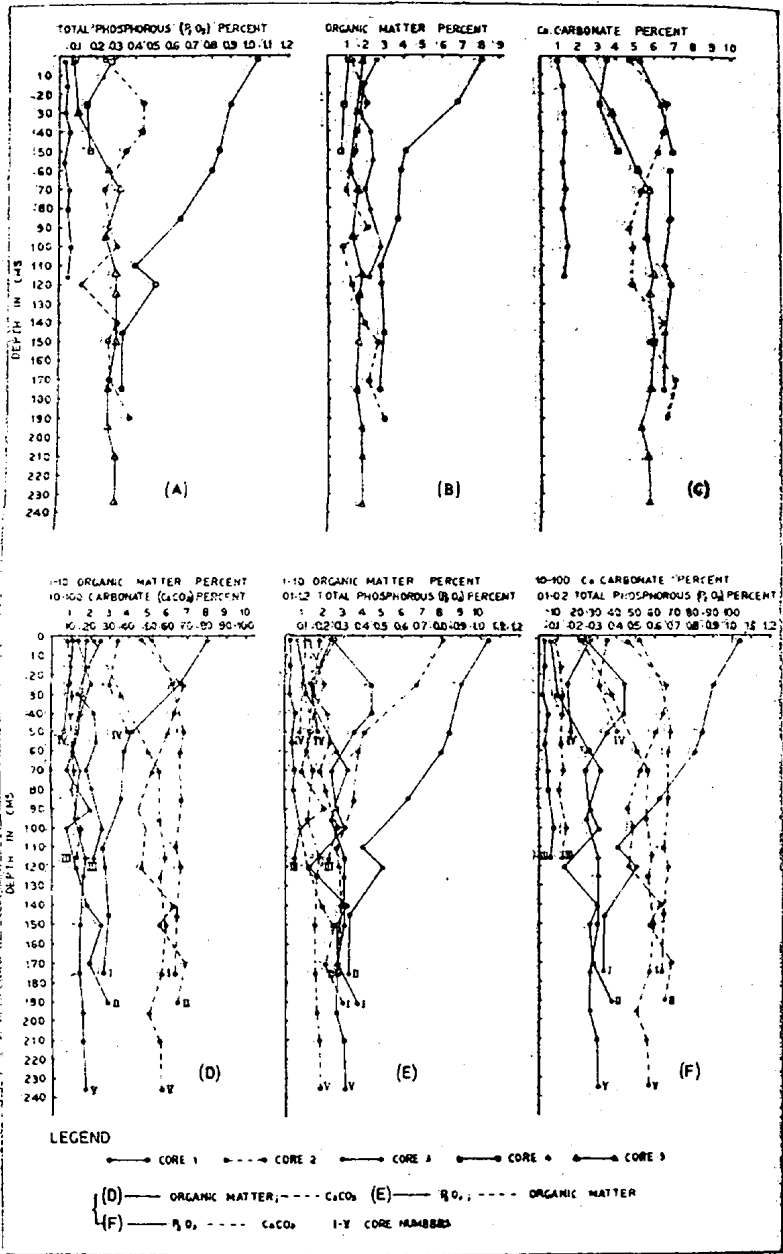


FIGURE 1 — Graphic representations of percentage distribution with depth in the sediment cores.

(A) Total Phosphorus (P₂O₅); (B) Organic matter; (C) Ca. carbonate; (D) Organic matter with Ca. carbonate; (E) Organic matter with Total Phosphorus (P₂O₅); (F) Ca. carbonate with Total Phosphorus (P₂O₅).

The average organic carbon here is 0.513%. In No. 5, organic carbon is again uniformly low, with very minor variations (except in sample No. 36) where sudden ecological variation sets in. Nevertheless, it is fairly uniform in the oolitic layer. The average organic carbon here is 0.904%, but for all the cores from the shelf it is 0.887%.

PHOSPHATE

At present, the total phosphorus (P_2O_5) deposition is highest (2,140-1,120 $\mu\text{g/gm}$ or 1.04-0.84% P_2O_5 , carbonate-free basis) in the uppermost 7.5-cm layer from the slope, and moderately high (720 $\mu\text{g/gm}$ or 0.25% P_2O_5) in the sediment-water interface portion in No. 4, and No. 2 (520 $\mu\text{g/gm}$ or 0.24% P_2O_5) from the basin. This contrasts with the low value in core No. 3 (105 $\mu\text{g/gm}$ or 0.025% P_2O_5) from the shelf off Bombay. No. 5 presents two opposing values (210 $\mu\text{g/gm}$ or 0.060% and 615 $\mu\text{g/gm}$ or 0.32% P_2O_5) consonant with the two different lithologies it represents. These values are for the top of the two layers. The averages are 0.640, 0.300, 0.042, 0.183 and 0.250% for 1-5 cores respectively, but for the shelf cores it is 0.160%, whereas it is 0.360% for Nos. 1, 4 and 5 only (all are on a carbonate-free basis).

The percentage values progressively decrease downward with depth in the slope cores, even though the oolitic fraction markedly increases downward. Nevertheless, these values are quite high. Phosphatisation in deeper waters (core No. 2) under lower temperature is extremely slow; however, the high values noticed are from oolitic and terrigenous fractions derived from the outer shelf/slope regions (samples Nos. 11, 12, 13, 15, 16, 19 and 21 in Table 1). Hence it may be surmised that the oolitic and other fractions, prior to deposition in the basin, were already phosphatised. Mero (1963, p. 70) also considers phosphate at greater depths (2,800 m off California, 3,800 m off South Africa, at the base of the slope) to be deposited by displacement, slumping and turbidity currents. The horizons of samples 10, 14, 17 and 20 show comparatively low values as they represent in-situ deposition. Of the three shelf cores No. 4 exhibits high values throughout, as expected from its lithology and the oxidising environment it represents. Similarly, according to Dietz *et al.* (1942) nodular phosphorite forming in Southern California results from primary precipitation in some regions occurring under oxidising conditions. Core No. 5 shows a progressive increase in phosphate with depth (in spite of varying lithologies), except at the time of the change in the environment (sample No. 36) and also when the deposition of detrital material ceased (samples Nos. 42 and 43). Phosphate values in core No. 3 are comparatively generally very low, although they are high at horizons immediately after the terrigenous inflow. This may possibly be due to dilution, to some extent, of euxinic conditions (Nos. 27, 28 and 29).

DISCUSSION

Marine phosphorite deposition through out geological time has been in marginal troughs or miogeosynclines (Cady, 1950), on adjoining cratons (Sheldon, 1964) or on platform facies with access to the open sea at one side (Degens, 1965) and in thalassocratic stages (Fairbridge, 1967). The present area of study, where phosphate deposition is considerable, has a similar geological setting and suites of rocks. Lithologically, the sediments are fine to coarse grained, and abundantly rich in phosphates, carbonates and organic matter (Setty, 1972 and Table 1, Fig. 1 A-F). They compare well with the depositional environment off Southern California (Dietz *et al.*, 1942) and in most respects with those of the phosphate deposits of Idaho and Turkey (Sheldon, 1964).

It is clear from Table 1 and Figure 1 (A-F) that there is a genetic relationship between phosphatisation and organic matter on the one hand and phosphatisation and carbonate deposition on the other. The organic carbon (C_{org}) closely fluctuates with the increase or decrease of phosphate and ranges from 4.655 with 1.04% P_2O_5 in the top of the core from the slope to 0.385 with 0.160% P_2O_5 in the bottom of the core from the shelf. It is also evident that abundance of organic matter under an anaerobic environment reduces carbonate deposition and that iron (Fe^{++}) is fixed as sulphide (FeS). Consequently the lack of iron to fix phosphorus as phosphate in the sediment will result in the low value for phosphate (No. 3, Kaplan and Rittenberg, 1963, p. 602). Also, it may be noted that the Eh effect most probably relates to its influence on the ferric to ferrous ratio which in turn controls the precipitation or solution of ferric phosphate (Rittenberg *et al.*, 1955, p. 41). The fine grain-size of the calcareous clayey matter and also clastic clayey material in a reducing environment increases phosphate values (No. 3). Coarseness of sediment grain size in No. 4, influenced by the introduction of clastic material, inhibits the accumulation of organic matter, hence low phosphate values. The high organic content in the sediment is directly related to the luxuriant organic productivity in the overlying surface waters and the abundance of nutrients brought in by upwelling. Upwelling and high organic productivity in the region has been reported by Carruthers *et al.* (1959), Sudarsan (1964), and Jayaraman and Gogate (1957). The close relationship of high organic matter in sediments and upwelling is found in the Channel Island area of California, and the west coasts of Panama, South America and equatorial Africa (Trask, 1939). Therefore, phosphate accumulates in nondepositional environments on the shelf (as in Nos. 4 and 5), partly on the slope (as in No. 1) and through the turbidites of shelf/slope in the basin (No. 2) of this region which are derived from the region of cores Nos. 1, 4 and 5. The conditions prevalent appear to be those required for phosphate deposition, such as upwelling, causing prolific organic productivity (Kazakov, 1937; Bushinski, 1964; Sheldon, 1964; Degens, 1965). The decrease of phosphate in Globigerina ooze horizons may be due to the ooze's positive Eh (Rittenberg *et al.*, 1955, p. 44).

The high values of phosphate in the cores are considered to be due to primary deposition and are not attributed to secondary enrichment either by leaching of associated carbonates or by replacement, because phosphorite deposition is very slow and is controlled by depth, pH and temperature. The absence of a decreasing trend of phosphate with depth in Santa Barbara basin is attributed to negative Eh and high pH (Rittenberg *et al.*, 1955 p. 39 and 43). In contrast, all the cores here (excepting Nos. 1 and 4) show a progressive increase. The same was reported for some cores off Southern California (Dietz *et al.*, 1942). Further, Emery (1960) has explained that tricalcium phosphate is precipitated from supersaturated solution, probably in the form of colloids, in upwelling waters. According to Krumbein and Garrels (1952), a high content of phosphate can be formed in restricted anaerobic basins with low pH only when conditions permit a removal of Ca^{++} as phosphate and where the activity product of calcium carbonate is not exceeded. Nos. 1 and 4 show a steady decline of phosphate with core depth. This correlates with the decline in organic carbon values and it may be partly attributed to bacterial utilisation, submarine weathering (Goldschmidt, 1962, p. 467) and phosphate being redissolved (depending on where the deposit is being formed). This view is in accordance with Krauskopf's (1967, p. 92) theory of direct and indirect modes of origin for phosphates.

The suite of rocks formed with all phosphorites are cherts, limestones and black shales; thus it may be stated that calcium carbonate is genetically

related. Further, it is known that solubility of calcium carbonate and calcium phosphate are mainly controlled by pH. According to Krumbein and Garrles (1952), there is coprecipitation of calcite and phosphate from a water saturated with Ca^{++} , CO_3^{-2} and PO_4^{-3} ions. It is this CaCO_3 which is partly leached and replaced by phosphate. According to Ames (1959) and Bushinski (1964), pre-existing CO_3^{-2} units of calcareous material are replaced by PO_4^{-3} units. Further it is suggested that Ca^{++} precipitation as carbonate or as phosphate chiefly depends upon the pH which controls the CO_3^{-2} ion concentration.

Carbonaceous matter is a common constituent in all the cores, but it is high where phosphate is also high. Sheldon (1964) considers that this is common with phosphorites which are associated chiefly with black shales in the phosphorites of the geological past.

CONCLUSIONS

(1) The per cent values and distribution pattern of phosphate, organic matter and carbonate present in the five cores indicate their close genetic relationship.

(2) Total phosphorus value is high in the core from the slope (No. 1) but almost uniform in those (Nos. 4 and 5) from the outer shelf and from the basin (No. 2). These values increase with depth except in No. 1 and 4.

(3) Values are very low in core No. 3 from the outer shelf, off Bombay which is from a euxinic environment and is considered to be from a 'closed basin' within the shelf.

(4) The organic carbon (C_{org}) fluctuates with increase and decrease of phosphate content in all the cores.

(5) Calcium carbonate values are uniform in the sediments from the slope and basin regions, but vary considerably in those from the shelf. Calcareous oolites are present throughout, except in one core (No. 3).

(6) It is clear that high phosphate is associated with high organic matter, which in turn is directly related to upwelling, luxuriant organic productivity, abundance of carbonate and a nondepositional environment.

(7) The shelf/slope region and the adjoining basin in the Bombay-Saurashtra coastal area seem to represent one of the localities where modern phosphorite deposits are now being formed.

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