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Calcium Phosphate Saturation in the Western Bay of Bengal

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Temperature, inorganic phosphate concentration and *p*H seem to be the major factors influencing the degree of saturation of calcium phosphate in sea water. Two water regions can be demarcated in the study area based on the saturation patterns of calcium phosphate. Distinct vertical and horizontal variations have also been observed in these waters.

Many forms of phosphorites occur in different parts of the World Oceans[1–3], but their chemistry of formation is still not well understood. Several theories have been put forth to explain their formation in the marine sediments and the 2 theories which gained considerable attention are (1) that they are formed by chemical precipitation[4,5] and (2) that they are incomplete replacement products formed from the pre-existing carbonate material[6].

The former has been widely accepted and is related to the solubility of the phosphate minerals in sea water[3,4,7–10]. Lack of data on the dependence of the degree of saturation on the physico-chemical characteristics of sea water and the variation of the apparent solubility product with these parameters, make it difficult to determine the absolute degree of saturation in sea water. In the present study an attempt has been made to determine the relative saturation in Western Bay of Bengal and to correlate its variations to physico-chemical characteristics of sea water.

Materials and Methods

Water samples were collected at different stations (Fig. 1) from standard depths up to 1500 m from hydrographic casts using transparent plastic Nansen water samplers (Hydrobios, Kiel, F.R.G.) and analysed for salinity, *p*H, temperature and inorganic phosphate using standard methods[11] and for calcium using the method of Culkin and Cox[12].

The degree of saturation is evaluated by estimating the ratio between the observed stoichiometric ionic product (IP)

$$IP = (Ca^{2+})^3\,(PO_4^{3-})^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

of the molar concentrations in sea water of the species involved and the apparent solubility product (K'_{sp})

$$K'_{sp} = (Ca^{2+})_S^3\,(PO_4^{3-})_S^2$$

in sea water under identical *p*H, temperature, pressure and salinity conditions. As a first approximation the degree of saturation is evaluated based on the value of $K'_{sp} = 4 \times 10^{-20}$ for sea water of ionic strength 0.84 at 20°C and 1 atmosphere pressure given by Kester and Pytkowicz[10]. The (PO_4^{3-}) concentration is calculated from the inorganic phosphate using the formula of Sendroy and Hastings[13].

$$PO_4^{3-} = \frac{T(PO_4)}{1 + \frac{aH^+}{K_3} + \frac{(aH^+)^2}{K_2\,K_3} + \frac{(aH^+)^3}{K_1K_2K_3}}$$

where $T(PO_4)$ is the inorganic phosphate concentration, aH^+ is the hydrogen ion activity and K_1, K_2 and K_3 are dissociation constants of phosphoric acid in sea water. The apparent dissociation constants of phosphoric acid for sea water tabulated by Kester and Pytkowicz[14] have been used.

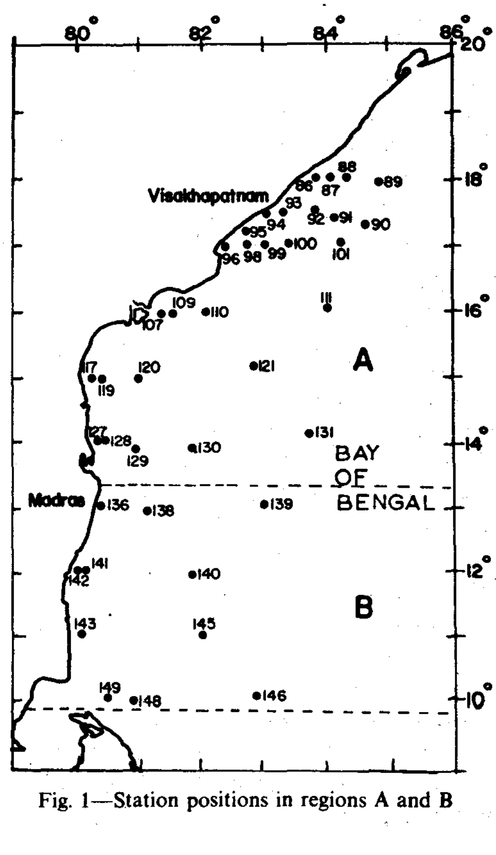


Fig. 1—Station positions in regions A and B

The percentage saturation is calculated for different depths of each station using the expression:

$$\text{Per cent saturation} = \frac{\text{IP}}{K'_{sp}} \times 100$$

Results and Discussion

The degree of saturation is essentially a function of calcium and inorganic phosphate concentration in sea water as seen from eq. 1. Calcium being a major element in sea water the normal variations in its concentration have a negligible effect on the ionic product. The important determining factor is trivalent phosphate which is a function of inorganic phosphate content, *p*H, temperature and salinity of sea water and the dissociation constants of phosphoric acid in sea water. The degree of saturation is discussed with respect to the above physico-chemical parameters.

The vertical and horizontal patterns of the degree of saturation in the present study show distinct variations. Based on the percentage saturation, inorganic phosphate concentration and *p*H the area under study can be divided into 2 regions (Fig. 1). Based on the same considerations both these regions can be broadly divided vertically into 3 layers (1) upper surface layer (0-50 m), (2) middle layer (50-150 m) and (3) deeper layer (150-1500 m). Integral mean values of inorganic phosphate concentration, *p*H and the percentage saturation are calculated at different layers and given in Table 1.

Region A shows a marked degree of undersaturation throughout the water column. The surface and the middle layers of region B are 3 and 2 times more saturated than the surface and the middle layer of region A respectively (Table 1). The varying degree of saturation of sea water is the combined effect of *p*H, inorganic phosphate concentration and also of temperature which shows a typical decreasing trend from surface to bottom. *p*H alone does not seem to be the controlling factor as observed by Kester and Pytkowicz[10]. Sea water being a complex system, the dissociation of phosphoric acid in this medium does not follow the same pattern as in other media[14]. Kester and Pytkowicz[14] found that K'_1 and K'_2 for sea water of 33‰ salinity are similar to those obtained from NaCl solution by Sendroy and Hastings[13] but K'_3 was 2 orders of magnitude larger in artificial sea water than in NaCl solution of the same ionic strength. Also the 3rd dissociation constant of phosphoric acid has a large temperature coefficient. This may probably be one of the reasons for the large variations in the degree of saturation of sea water at different depths. The magnitude of the effect of pressure on the dissociation constants of phosphoric acid and the solubility of calcium phosphate cannot be emphasised at present.

Table 1—Integral Mean Values of *p*H, Phosphate and Per Cent Saturation at Different Depth Intervals in Bay of Bengal

Depth m	*p*H	Inorganic phosphate-P $\times 10^6$ moles/litre	Per cent saturation
Region A (18°-13°N)			
0-50	7.85	0.68	45.3
50-150	7.74	1.35	52.4
150-1500	7.59	2.92	10.7
Region B (13°-10°N)			
0-50	7.88	1.16	142.9
50-150	7.75	2.09	104.8
150-1500	7.58	3.08	13.1

The surface and the middle layer of both the regions have almost identical *p*H. High degree of saturation in both these layers of region B seems to be the result of higher inorganic phosphate concentration encountered. The temperature difference is not very significant to cause such a change. The higher percentage saturation in the middle layer is due to the higher concentration of phosphate as compared to the surface but the values did not show the expected increase in the saturation due to suppression by the low *p*H and temperature. The middle layer being thermocline layer, the temperature variations are quite significant causing considerable variations in the percentage saturation. *p*H is also lower in this layer as compared to that at surface (Table 1).

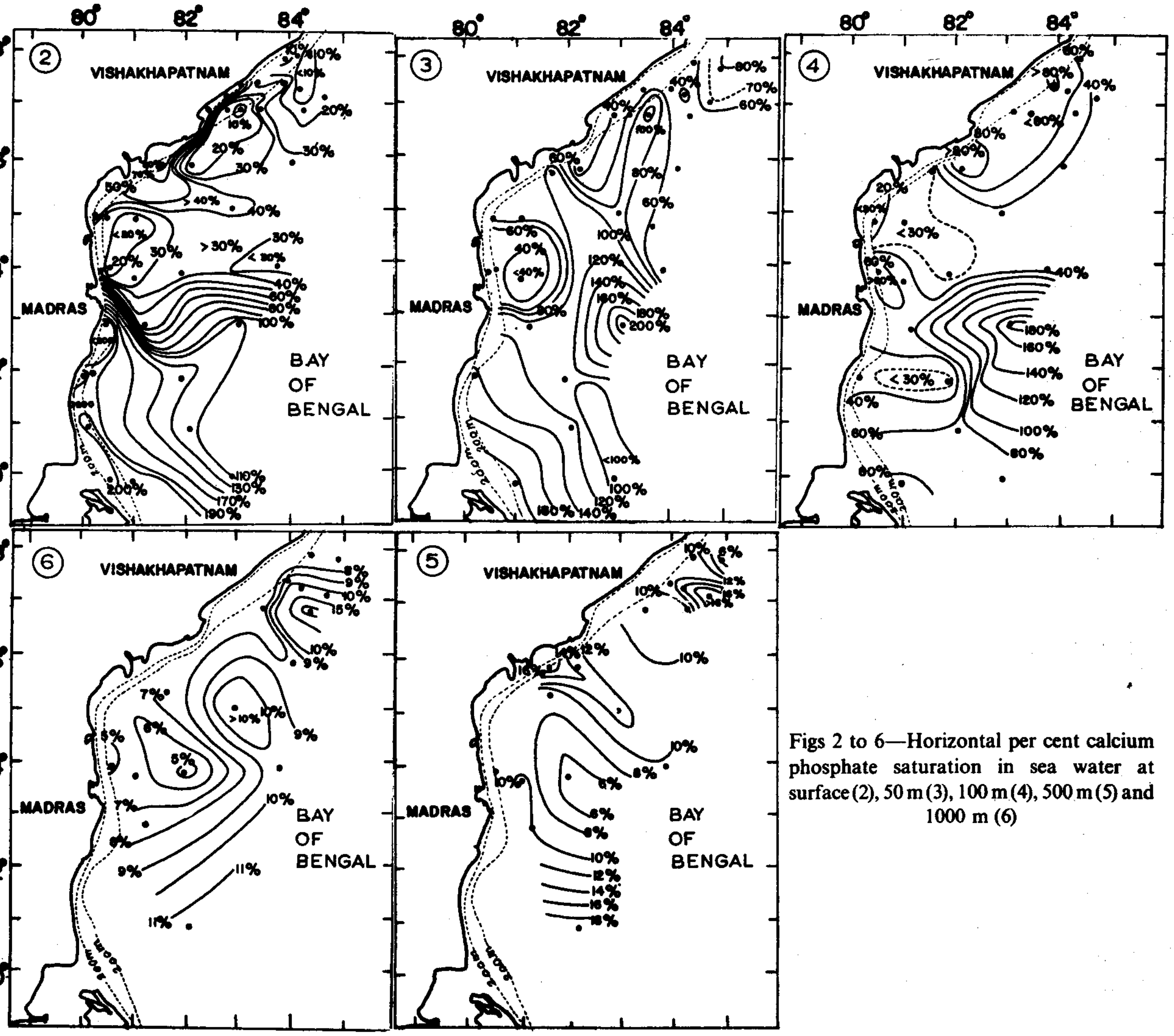
The percentage saturation of the deeper layers is almost the same in both the regions. Though the concentration of inorganic phosphate is higher in this layer, low temperature associated with low *p*H seems to allow only a small fraction of the total inorganic phosphate to be present in the trivalent form. The decrease in the concentration of PO_4^{3-} leaves the bottom water highly undersaturated with calcium phosphate.

Kester and Pytkowicz[10] in their study of the relative calcium phosphate saturation in the 2 regions of the North Pacific Ocean observed that the sea water in the basins off Southern California is about 5 times more saturated than those further North. They used the data of Rittenberg *et al.*[15] in the basins off Southern California at depths between 800 and 1200 m. The average *p*H in this water was 7.73 and the inorganic phosphate concentration was 3.22×10^{-6} moles/litre. The temperature was 4-5°C. *p*H and inorganic phosphate concentration at similar depths in the Bay of Bengal water are 7.58 and 3.08×10^{-6} moles/litre respectively. The temperature was 5-7°C. Comparison of present data on *p*H and inorganic phosphate with that in the Southern California basins indicates that the difference in the degree of saturation is mainly due to the difference in *p*H since the total inorganic phosphate concentration is more or less same and the effect of the difference in temperature is negligible.

In general the spatial distribution of percentage saturation of calcium phosphate in the coastal and offshore waters is determined mainly by the prevailing levels of inorganic phosphate, *p*H and temperature.

Horizontal profiles of saturation—Surface (Fig. 2): In the surface waters the degree of saturation increases from north to south. Region A shows varying degrees of undersaturation ranging from 10% towards the north of Visakhapatnam to about 40% between Visakhapatnam and Madras. A higher degree of saturation is observed in the coastal waters of Visakhapatnam, with a decreasing trend away from the coast. This is attributed to the higher concentration of inorganic phosphate near the coast. The phosphate concentrations at stations near the coast varied from 0.33×10^{-6} to 0.66×10^{-6} moles/litre, except at sts 94, 95 and 96 where the average concentration is 0.92×10^{-6} moles/litre. The surface *p*H in the coastal stations does not show any significant difference from those in the offshore. A possibility of upwelling in this region has been suggested[16] which may be responsible for the differences in the inorganic phosphate concentration and consequently on the percentage saturation. A greater degree of saturation with increase towards the coast south of Madras is again due to the effect of higher inorganic phosphate concentration. The phosphate concentration at stations near the coast varied from 0.93×10^{-6} to 1.59×10^{-6} moles/litre whereas away from the coast it varied from 0.66×10^{-6} to 0.99×10^{-6} moles/litre. The high inorganic phosphate in this region also may be due to upwelling. Upwelling during this period along the east coast of India off Visakhapatnam and Madras has already been reported[17].

50 m (Fig. 3): At 50 m also an increasing pattern from north to south is observed. Region A shows a higher



Figs 2 to 6—Horizontal per cent calcium phosphate saturation in sea water at surface (2), 50 m (3), 100 m (4), 500 m (5) and 1000 m (6) degree of saturation compared to the surface. The degree of saturation increases from the coast to the offshore off Madras, whereas it shows a reverse pattern south of Madras. The increasing degree of saturation towards offshore off Madras is due to increasing *p*H, temperature and inorganic phosphate concentration. Higher *p*H which might be related to high productivity seems to be mainly responsible for the increasing trend of saturation towards the coast south of Madras.

100 m (Fig. 4): At this depth the water near Visakhapatnam shows almost the same degree of saturation as at 50 m. The increasing saturation towards the coast is due to increasing phosphate. A very low degree of saturation (< 20%) is observed towards north of Madras. The sea water in this region is associated with high inorganic phosphate and low *p*H. *p*H seems to be the controlling factor in this region. Off Madras the same distribution pattern is observed as at 50 m.

500 m (Fig. 5) and 1000 m (Fig. 6): Percentage saturation at these depths is very low (5-18%) and the pattern of distribution is similar. In general, the values in the region A are more or less same at both the levels. However, in the region B the values at 500 m are slightly higher than at 1000 m reaching maximum south of Madras. The poor degree of saturation at these depths is obviously the influence of low temperatures and *p*H.

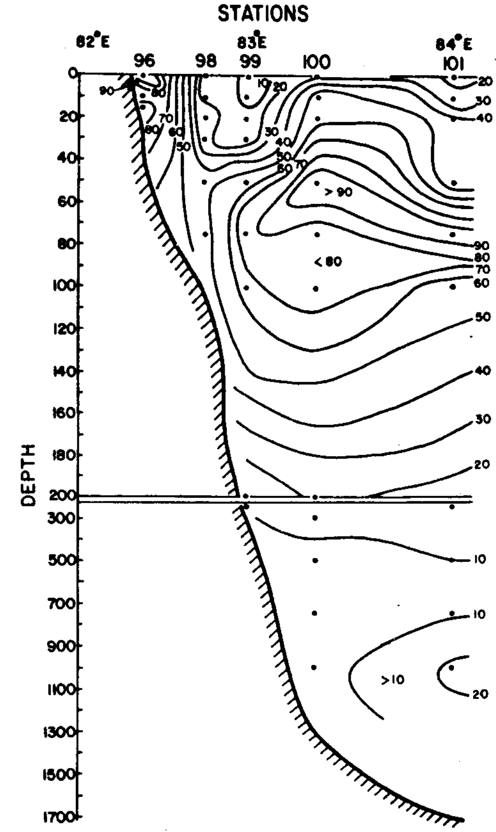


Fig. 7—Vertical per cent calcium phosphate saturation in sea water between 82-84°E long. in Bay of Bengal

Vertical profile of saturation—The degree of saturation for stations in region A increases from surface to about 80 m (Fig. 7). The maximum saturation being 90% at this depth. Below 80 m the percentage saturation tends to decrease with depth. The high saturation (> 50%) observed between 50 to 130 m is attributed to the near optimum combinations of *p*H, inorganic phosphate and temperature conditions at these depths. It is also significant to note that at the coastal st 96 the per cent saturation is maximum (80-90) over the entire water column as compared to the offshore (< 50).

Thus there is a high degree of variability in the saturation levels with respect to region and depth. It may be mentioned here that the reliability of the degree of saturation of sea water with calcium phosphate depends on the closeness of the dissociation constant values to the actual values in sea water. Especially at deeper layers (< 500 m) the deviation in the percentage saturation may be quite significant since the dissociation constants used in the present computations could be different from the actual constants due to high pressures involved. The apparent solubility product given by Kester and Pytkowicz[10] has been calculated at 20°C and the same has been used for all temperatures. At greater depths where sea water is much colder this value may not be very correct. Also the effect of pressure and temperature on the solubility of calcium phosphate is not known. Despite these limitations, the present account gives a reasonable picture about the calcium phosphate saturation pattern. Since the major factors controlling the saturation are *p*H, temperature, salinity and inorganic phosphate, in future emphasis should be made to study the apparent solubility product (K'_{sp}) under different sea water conditions to achieve higher degree of accuracy.

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