Origin and significance of high-grade phosphorite in a sediment core from the continental slope off Goa, India

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A phosphorite crust was found at 380–390 cm depth interval of a sediment core collected from the topographic high occurring on the continental slope off Goa. This crust is fragile and grey to light brown in colour. Carbonate fluorapatite is the predominant mineral followed by minor pyrite. Thin section studies indicate that it is mostly homogeneous with a few bone fragments and shows porous microstructure. SEM studies show that it contains agglomerated 1–2 μm size apatite globules resembling phosphatized bacteria and coalesced bacteria. Microprobe geochemistry of the phosphorite indicates that it contains 33% P_2O_5 and 50% CaO with other major elements (Si, Al, Ti, Fe, Mg, Na and K) amounting to only 1.8%. The mode of the phosphorite crust formation is discussed in relation to Quaternary phosphorites in upwelling and non-upwelling regions. It is suggested that the initial substrate for the phosphorite crust was most probably a fish coprolite which phosphatized under lower rates of terrigenous sedimentation and calm environmental conditions during the Pleistocene.

IN phosphorites the P_2O_5 content generally exceeds 18% and it may sometimes reach up to 40%. Phosphorites with higher P_2O_5 content are not only of scientific interest but are also of significant economic value. So far, phosphatized limestones consisting of 2–14% P_2O_5 (bulk analyses)[1–5], the sediments[6] with 0.2–2.0% P_2O_5 and glaucony-phosphate facies associated sediments[7] were reported from the western continental margin of India. In this paper, we report the origin and significance of high-grade phosphorites (34% P_2O_5) sporadically occurring at subsurface depths of the sediment cores collected from the topographic high on the continental slope off Goa.

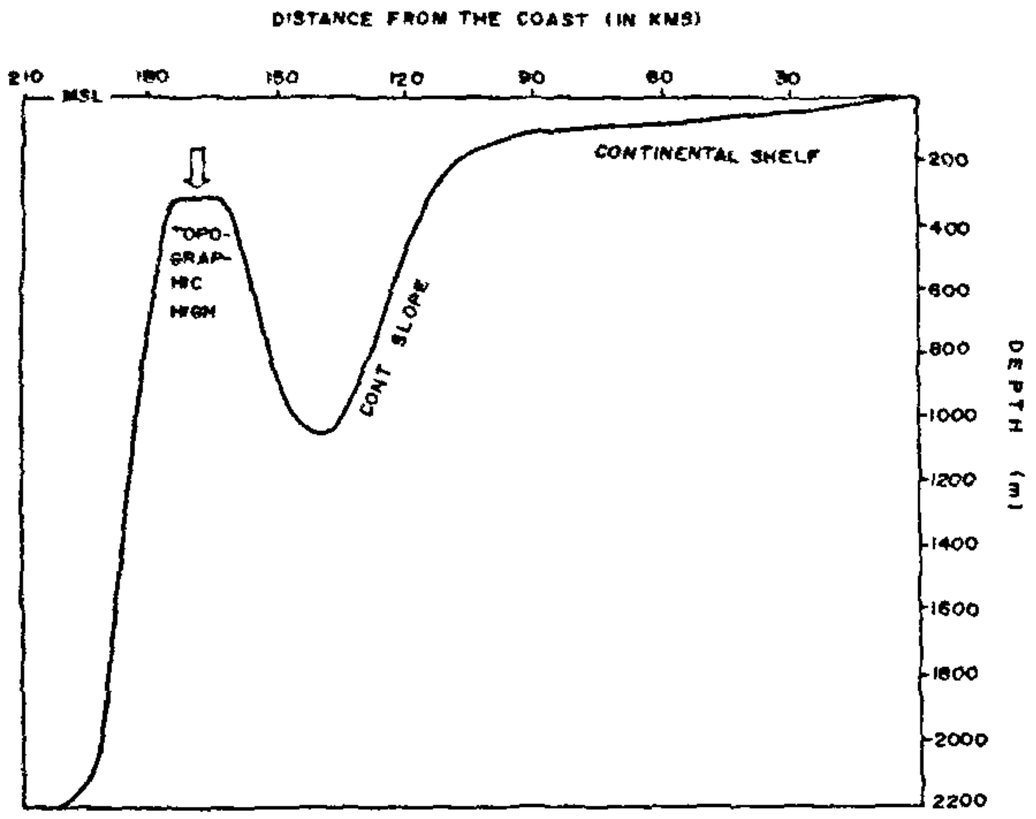

Figure 1. Schematic cross section of the continental margin off Goa showing topographic high on the continental slope; arrow shows the core location (data provided by Dr M. Veerayya).

As a part of Institute's geological exploration programme, more than 30 sediment gravity cores were collected on the western continental margin of India (in the year 1993–94) during different cruises of *O R V Sagar Kanya* and *A A Siderenko*. Most of these cores are from the central and southwestern margin where intense seasonal upwelling has been reported. These cores are distributed at water depths between 20 m and 2000 m and thus are located above, within, and below the oxygen minimum zone (150–1500 m). During subsampling the sediment cores onboard, phosphorite nodules/crusts were found only in three gravity cores collected from the topographic highs occurring on the continental slope off Goa (Figure 1). These phosphorites occur sporadically at one or two sediment intervals at deeper subsurface depths of the cores. All these phosphorites contain about 34% P_2O_5. In the remaining cores there are no phosphorites except a few phosphate grains occurring as traces at different sediment intervals.

The phosphorite crust studied here is from a 4.3 m long gravity core (GC-2) collected on the topographic high in 330 m water depth off Goa (Figure 1) (14°49.6′N, 72°38.8′E) during the VI cruise of *A A Siderenko*. This crust is found at 380–390 cm depth interval of the core. The phosphorite crust is about 3.5 cm long and somewhat flat with thickness of about 1.5 cm (Figure 2 *a*). It is grey on one side and light brown on the other. It is friable and similar to F (friable)-phosphates reported by Garrison and Kastner[8]. Both the surfaces show grooves (Figure 2 *a*) and small boring cavities, indicating that it was indurated under hardground conditions. Bulk mineralogy by X-ray diffraction (Figure 3) shows that the carbonate fluorapatite is the only mineral phase. Pyrite, however, occurs in acid insoluble residue. The bulk chemistry analysed by ICP-AES shows that the crust consists of about 34% P_2O_5 and 49% CaO. The major element geochemistry of the phosphorite, analysed by microprobe, significantly differs from that of the Modern/Quaternary phosphorite nodules/crusts in other upwelling/non-upwelling regions (see Table 1) and consists of more P and Ca and very low content of other major elements. Bone fragments contain relatively less P_2O_5 than the matrix (Table 1).

Thin section of the phosphorite indicates that it is mostly homogeneous with a few scattered bone fragments and fish remains and shows porous structure (Figures 2 *b*, *c*). Pyrite occurs as small black grains. The bones are susceptible to degradative transformation and show different stages of phosphomicritization (Figures 2 *d*, *e*). Some bones are partly micritized (Figure 2 *e*) and others are completely micritized and transformed into undifferentiated peloids (Figure 2 *f*). Elsewhere, the bones are surrounded by black material of possible organic origin. SEM observations on freshly broken surfaces of the phosphorite attest the thin section findings. It consists of abundant porous microstructure with adjacent moderately compacted areas (Figure 4 *a*). Within the porous area, apatite everywhere occurs as agglomerated globules of different size (0.5–2 μm) (Figure 4 *b*). These globules resemble phosphatized bacteria and coalesced bacterial structures[9,10]. The compact areas seem to correspond to thick coalescence of globules and globule aggregates. Figure 4 *c* shows the pyrite aggregate composed of many cubes and octoids of pyrite and porous apatite structure corresponding to globules.

The sediments of the core are clayey at the surface and up to 40 cm depth of the core and clayey sand/silty sands occur below. The organic carbon content in the upper 40 cm of the core is high (about 8%) and in the remaining core, it ranges from 0.8 to 3.7%, with an average value of 1.0%. In contrast, the calcium carbonate content is low (up to 43%) in the upper 40 cm and increases down core with values ranging from 60 to 80%. Coarse fraction studies indicate that in the upper part of the core, planktonic foraminifers show solution features and contain several keels of planktonic foraminifers and pyrite encrusted/infilled foraminifers. In the remaining part of the core, the coarse fraction consists of abundant planktonic forams, pteropods, shell fragments, molluscs and otoliths distributed more or less uniformly in the core. Corals encrusted on a small gastropod shell (Figure 5) were found at a sediment interval 360–370 cm), close to that of phophorite depth interval (380–390 cm).

Some of the Modern phosphorites (off Peru and SW Africa) occur in upwelling regions[11,12], while others (Eastern Australia phosphorites) are in weak/non-upwelling regions[13]. As the western margin of India is concerned, (a) intense seasonal upwelling occurs on the southwestern continental margin of India, (b) organic carbon values range from 3–16% in the surficial sediments of the continental slope[14] and up to 8% in the

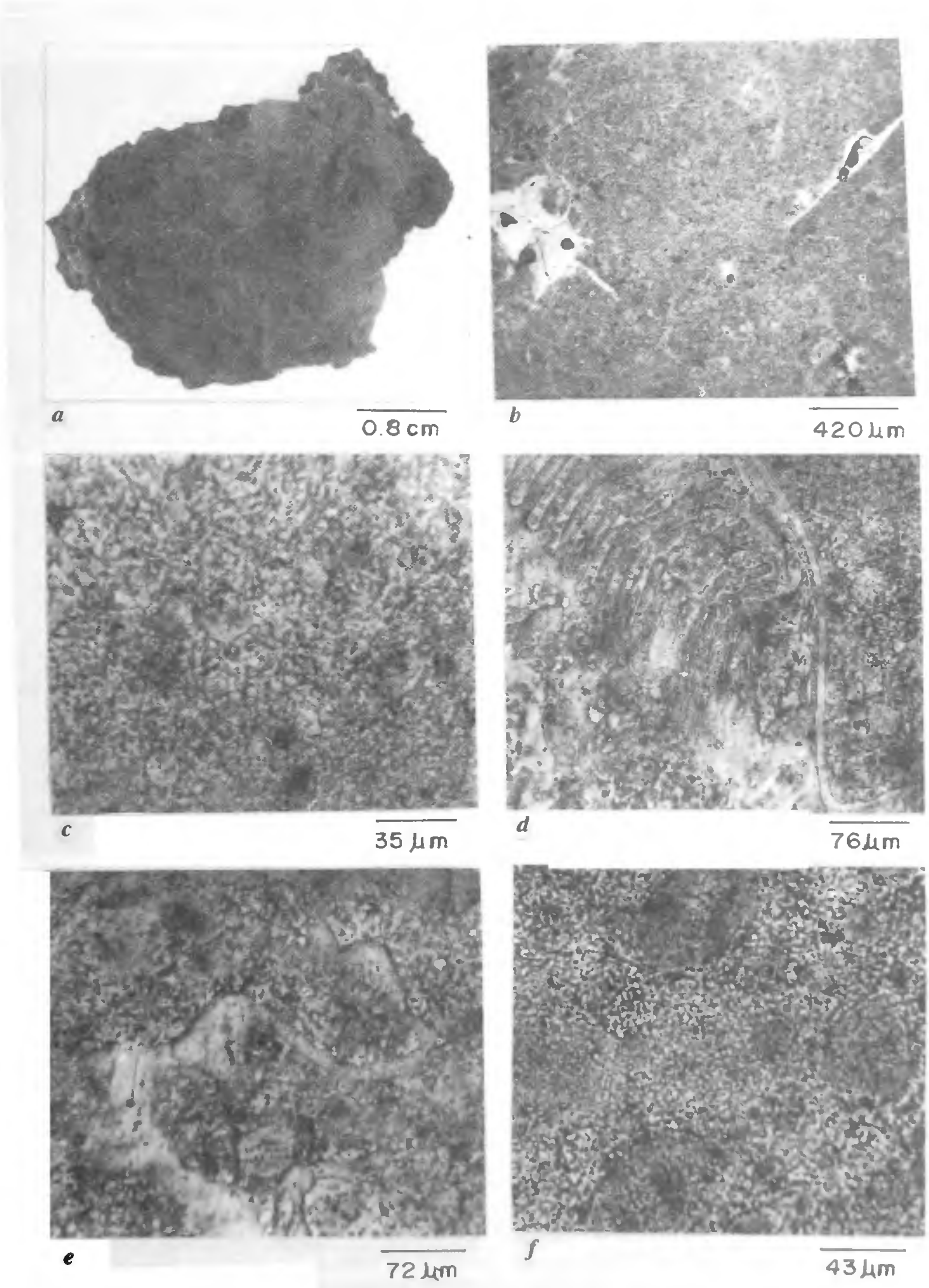

Figure 2. *a*, Phosphorite crust, (*b–f*) are thin section photomicrographs; *b*, at low magnification showing homogeneous apatite structure with a few bone fragments; *c*, high magnification showing porous microstructure, *d*, fish bones being micritized, *e*, bone fragment showing phosphomicritization; *f*, the end product of phosphatization of bones showing undifferentiated phosphate peloids

Table 1. Geochemistry of the phosphorite and their comparison with modern phosphorite nodules from other regions

			Modern phosphorites from		
	Phosphorite crust from the Indian margin (upwelling region)		other upwelling regions		weak/non-upwelling region
Element	1 (15)*	2 (3)	3 (21)	4 (46)	5 (4)
SiO_2	0.11	0 06	8.79	19.39	24 00
Al_2O_3	0.33	–	2.68	1.95	3.53
TiO_2	0.03	0.03	ND	ND	ND
FeO	0.39	0 13	1.28	6.95	4 50
MnO	0 02	0.01	ND	ND	ND
MgO	0 81	0 52	0.99	1.41	1.31
CaO	50.17	49.00	42 00	37.28	31 90
Na_2O	–	–	1 08	0.90	0.90
K_2O	0.10	0 12	ND	1.38	0.89
P_2O_5	33.26	30.72	27.58	17.42	11.00

* Average of number of analyses, ND – not determined,
1 & 2 This study, microprobe analyses of phosphorite crust from the western margin of India; 1. analyses of matrix; 2. analyses of bone fragments.
3 Phosphorite nodules from Peru margin (microprobe analyses)[11].
4 Phosphorite nodules from Namibia (microprobe analyses)[12].
5 Eastern Australian margin non-ferruginous phosphorite nodule[26].

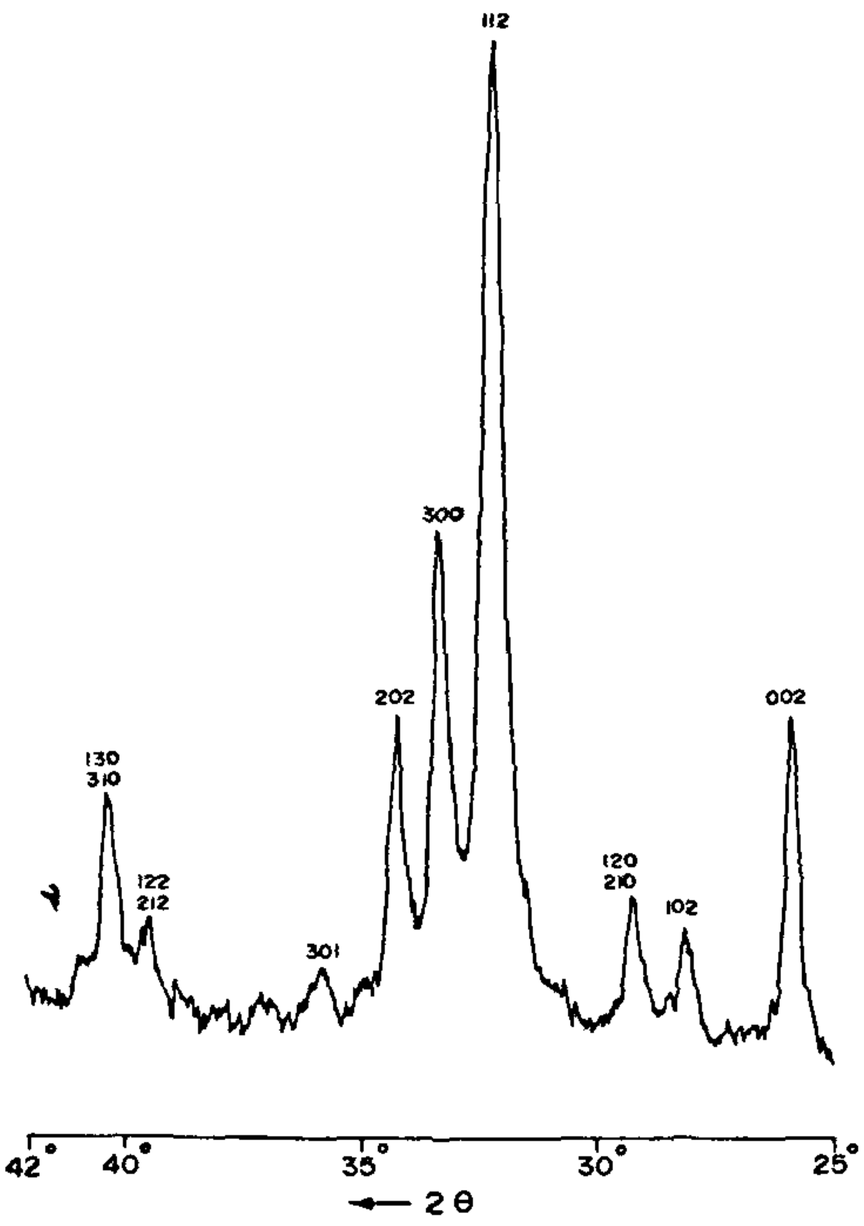

Figure 3. X-ray diffractogram of the phosphorite (bulk analysis), showing all the reflections are due to carbonate fluorapatite.

upper 1 m sediments of the gravity cores (M. Thamban, unpublished work) and are comparable to the organic carbon values of the Peru and SW African margins and (c) oxygen minimum zone (150–1500 m) intersects the continental slope. In spite of all ((a)–(c)) these upwelling-induced conditions, phosphorites have not been observed in the upper one meter sediments of all the thirty gravity cores. We, therefore, suggest that just having upwelling is not sufficient enough to produce phosphorites. Glenn *et al.*[15] recently reviewed the environmental conditions for phosphorite formation and suggested the influence of several factors on phosphogenesis. As the sediments in the cores are carbonate-rich, carbonate ion concentrations in the pore waters[16] and rate of sedimentation are probably major controlling and inhibiting factors for the formation of modern phosphorite in this margin.

Modern/Quaternary phosphorites mostly occur in the form of nodules/crusts. The initial substrate (host) for phosphorite is part of sediment and obviously the phosphorite nodule/crust is heterogeneous and contains partly replaced and/or unaltered sediment constituents such as diatoms, foraminifers, quartz, clay minerals, etc. The geochemistry of this type of diagenetic nodules/crusts is shown by higher contents of other major elements along with higher P values (see Table 1) supporting the existence of sediment constituents. Although the calcareous skeletal dominated sediments are associated with the phosphorite under investigation, it neither contains carbonate skeletals nor other sediment constituents except bone fragments (Figure 2). Geochemistry also shows higher P and Ca values and very low content of other major elements than the modern phosphorite nodules/crusts (see Table 1). These suggest that the host substrate for phosphorite may not be the associated sediment. Similarly, based on petrography, we suggest that the host substrate in our phosphorite is not identical to those in pelletal phosphorites[17] and phosphatized microstromatolites[18].

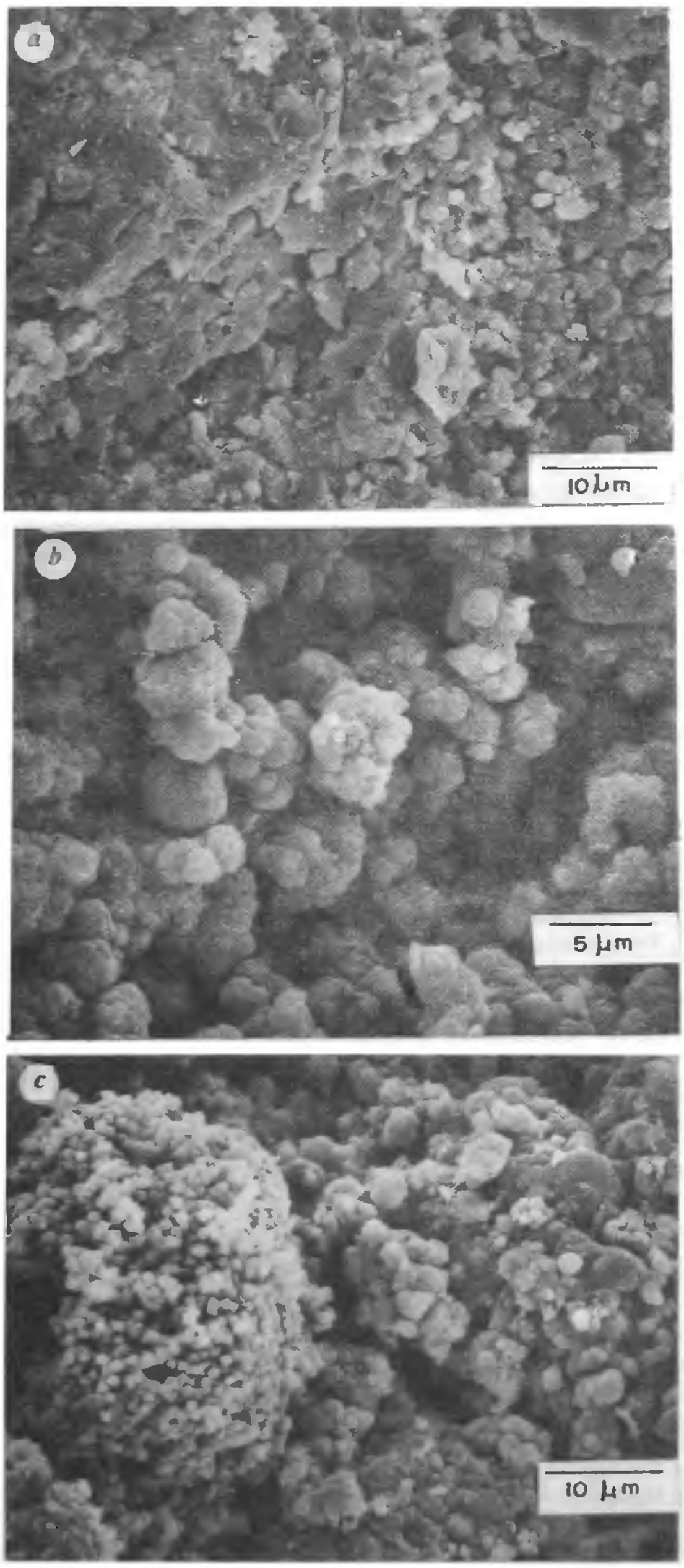

Figure 4. *a–c*, SEM photographs. *a*, apatite microstructure with moderately compact area with adjacent porous areas. *b*, porous area showing agglomerated apatite globules resembling phosphatized bacteria. *c*, Pyrite aggregate showing cubes and octoids of pyrite with adjacent area showing porous apatite microstructure corresponding to globules.

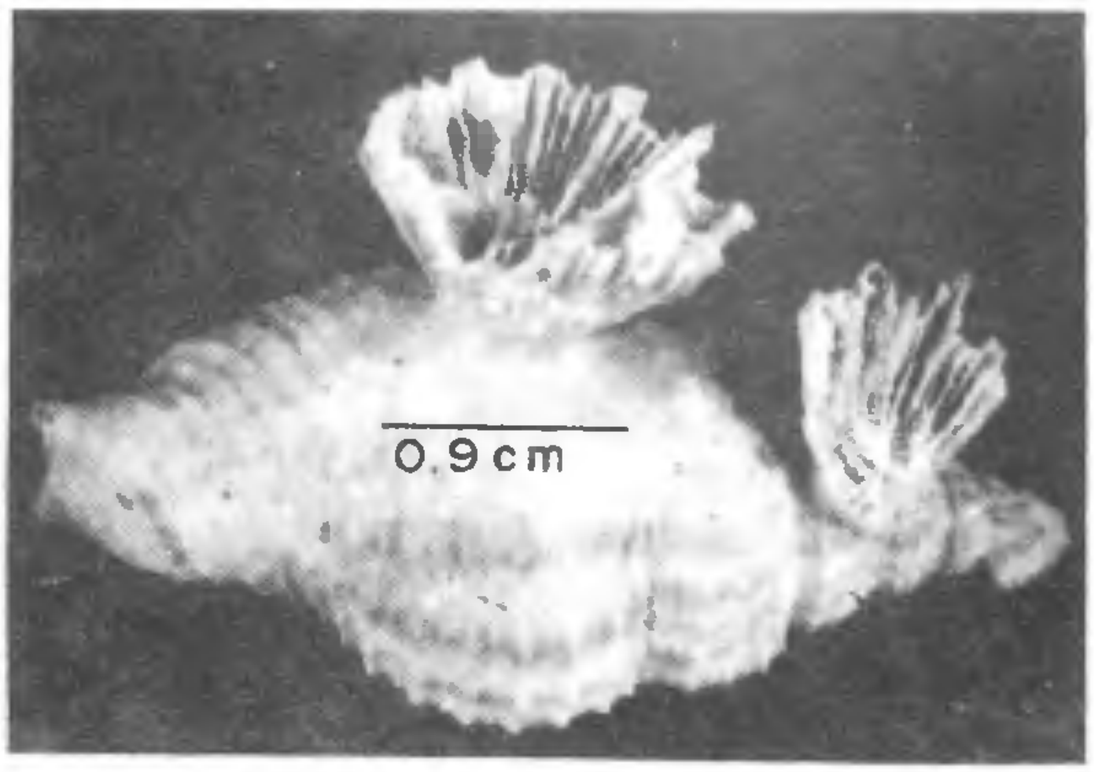

Figure 5. Photograph showing corals encrusted on a small gastropod shell.

The only possibility is that the initial substrate for the phosphorite crust may be a coprolite. Cayeux[19] described coprolites which show typical homogeneous and porous microstructure with few fish remains. More recently, Lamboy[20] reported copronodules from ODP cores of the Peru margin. Subsequent studies[9,10] have documented the homogeneous nannostructure of fish coprolites from various phosphorites including those from the ODP cores of the Oman margin. The observations in our phosphorite are in good agreement with the reports of these workers. It has been suggested that the faeces of carnivores contain highest P_2O_5 content (up to 11%) as they contain undigested remains of bone material and, those of herbivores seem to contain not more than 0.2–0.4% P_2O_5 (cf Slansky[21]). We therefore suggest that the initial excrement may belong to carnivore fishes and become phosphatized. The phosphorite thus produced subsequently became flat due to the overburden of sediment. Absence of hydroxyl apatite reflections in X-ray diffractogrammes, in spite of the existence of bone fragments and fish remains, may be due to the fact that the replacement of hydroxyl ion of the bone by fluoride ion is an ion exchange process and does not require major chemical alteration[21] and/or the total hydroxyl apatite in the sample is <5%.

The precise mechanism of apatite precipitation in coprolites is not known but may be similar to the one reported for authigenic minerals. (a) The major sources for phosphate were most probably the P released during early diagenetic degradation of organic matter and bone fragments associated with the initial excrement. (b) It is also known that dense populations of microbes inhabit the intestines of living vertebrates and their faeces normally contain abundant bacteria[22]. The presence of only agglomerated microspheres (Figure 4*b*) resembling

phosphatized bacteria everywhere in the phosphorite may indicate the confined environmental conditions favouring the growth of only one type of microbial group. (c) The associated sediments do not contain pyrite whereas, the phosphorite crust contains several pyrite grains implying that the initial excrement itself may have acted as a restricted suboxic/anoxic microenvironment. In view of (a)–(c), we suggest that the microbes existing within the initial excrement assimilated P and F from within and also from the overlying waters, precipitated carbonate fluorapatite and phosphatized only coprolite in the confined microenvironmental conditions.

The initial excrements of fish are very fragile and may rapidly disintegrate with any small disturbance. The initial excrement was survived, phosphatized and indurated into a crust implying that very calm environmental conditions must have existed at the site during phosphatization. Growth of corals on a small gastropod shell (Figure 5) occurs close to the sediment interval of phosphorite crust. The transportation of these corals from elsewhere is ruled out as the sediment core under study was taken from a topographic high, an isolated feature on the continental slope (Figure 1). The encrustation of coral even on a small gastropod shell implies the prevalence of quiet conditions and low rates of terrigenous sedimentation. These conditions thus corroborate the phosphatization conditions of coprolite.

As the phosphorite crust is not occurring in upper 50 cm of the core, it is not a modern phosphorite. The age of the sediments in the core depends on the rates of sedimentation. The rate of sedimentation on the continental slope is about 4 mm/yr (ref. 23); these rates, however, cannot be used for our core as it was taken from a topographic high. Colour and texture of the sediments, organic carbon and calcium carbonate contents of the sediments significantly differ and vary in the sediments of the upper 40 cm of the core and the sediments below. This depth representing changing sedimentary conditions may correspond to Holocene/Pleistocene boundary. The sediment cores collected in the vicinity (Laccadive Sea) also showed similar sedimentary change at about 40 cm depth interval and based on the radiocarbon dates this depth interval has been suggested as Pleistocene/Holocene transition[24]. The rate of sedimentation during the Pleistocene was apparently low as evidenced by the phosphorite and coral encrusted gastropods at different levels. Even if we apply average sedimentation rate (2.2 cm/10^3 yr) recorded in the adjacent Arabian Basin[25], the sediments at 380–390 cm (phosphorite) interval might have deposited during the upper Pleistocene.

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