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Phosphorite concretions in a sediment core from a bathymetric high off Goa, western continental margin of India

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A sediment core collected from a bathymetric high off Goa on the western continental margin of India, has yielded phosphorite concretions with an average P_2O_5 content of 32.75%, the P_2O_5 concentrations being highest ever reported from the margins of India. These concretions vary in size from < 1 to 5 cm, are subrounded, oval to irregular in shape, dark grey to yellowish grey in colour and consist of carbonate fluorapatite (CFA) as the single mineral phase. The concretions are present in the sediments at various levels below 110 cm from the core top and appear to be older than at least 250,000 yrs. Our study indicates that the phosphate released into the interstitial water due to decomposition of organic matter and dissolution of fish debris is precipitated as microgranular phosphorites which are consolidated and progressively become concretions with time.

PHOSPHORITES are generally found in diverse geographic and physiographic settings in marine environment. Modern phosphorites are reported from the continental margins of Namibia and Peru–Chile, in association with diatomaceous ooze and organic matter-rich sediments where coastal upwelling is strong^{1–5}. On the other hand, phosphatic nodules of Quaternary and Neogene ages occur in organic-poor sediments on the shelf off eastern Australia, an area known for its weak upwelling^{6–8}. Several workers have reported the occurrence of marine phosphorites in the Indian Ocean^{9,10}. On

the western continental shelf of India, phosphatized algal limestones of Holocene age have been reported^{11–13}. The average P_2O_5 content of these phosphorites is less than 10% (ref. 13). In this paper we report the occurrence of phosphorite concretions, with an average P_2O_5 content of 32.75%, in a 5.85 m long core collected in the water depth of 320 m from the summit of a bathymetric high, off Goa, western continental margin of India.

The core consists of light olive grey to olive grey coloured siltyclays and clay-bearing calcareous oozes, along with organic-rich biogenic carbonate sediments and fish debris, mostly hemipelagic in nature. Other sedimentary facies conspicuous in the core are phosphatic concretions. Phosphorite concretions are distributed at various levels in the core below 110 cm (Figure 1). They are dark grey, yellowish grey and light yellow and subrounded, oval or irregular in shape with a size range of < 1 to 5 cm. Their surfaces are rough with small depressions and cracks (Figure 2). The larger concretions were hand-picked during subsampling onboard, while smaller ones were separated through wet sieving (230 μ m mesh). The concretions were washed with distilled water, dried at < 50°C till all the moisture was removed, powdered in an agate mortar and analysed for mineralogical (X-ray diffraction) and chemical composition [Inductively coupled plasma atomic emission spectrometry (ICP-AES)]. Major oxide geochemistry was determined by electron probe micro analyser (EPMA). Polished sections and freshly broken parts of several concretions were studied using scanning electron microscope (SEM) for microstructures and minerals present in it. Thin sections of representative samples were studied under petrological microscope.

The only mineral phase identified in the X-ray diffraction analysis of these concretions (Figure 3) is pure carbonate fluorapatite (CFA). Other minerals such as quartz, feldspars, glauconite, pyrite, dolomite and clay minerals, generally associated with phosphorites^{3,14} are not found in these samples. SEM studies reveal that the voids between CFA crystallites are not filled with any detrital and/or diagenetic minerals (Figure 4). Petrological study of thin sections also confirms that the concretions consist of only CFA phase, devoid of any other minerals. P_2O_5 content in the concretions range between 30.90 and 33.91% with an average value of 32.75% and CaO content from 52.82 to 55.15% with an average value of 54.15%. The CaO/ P_2O_5 ratio varies between 1.56 and 1.78 with an average of 1.65. EPMA analysis reveals that the composition is similar both at inter-concretional and intra-concretional levels. The P_2O_5 content in these concretions is much higher than the reported value (highest average value for the outer layers = 9.5%) for phosphatized algal nodules of western shelf of India¹³. Comparisons of offshore phosphorites from various locations (Table 1) indicate that the

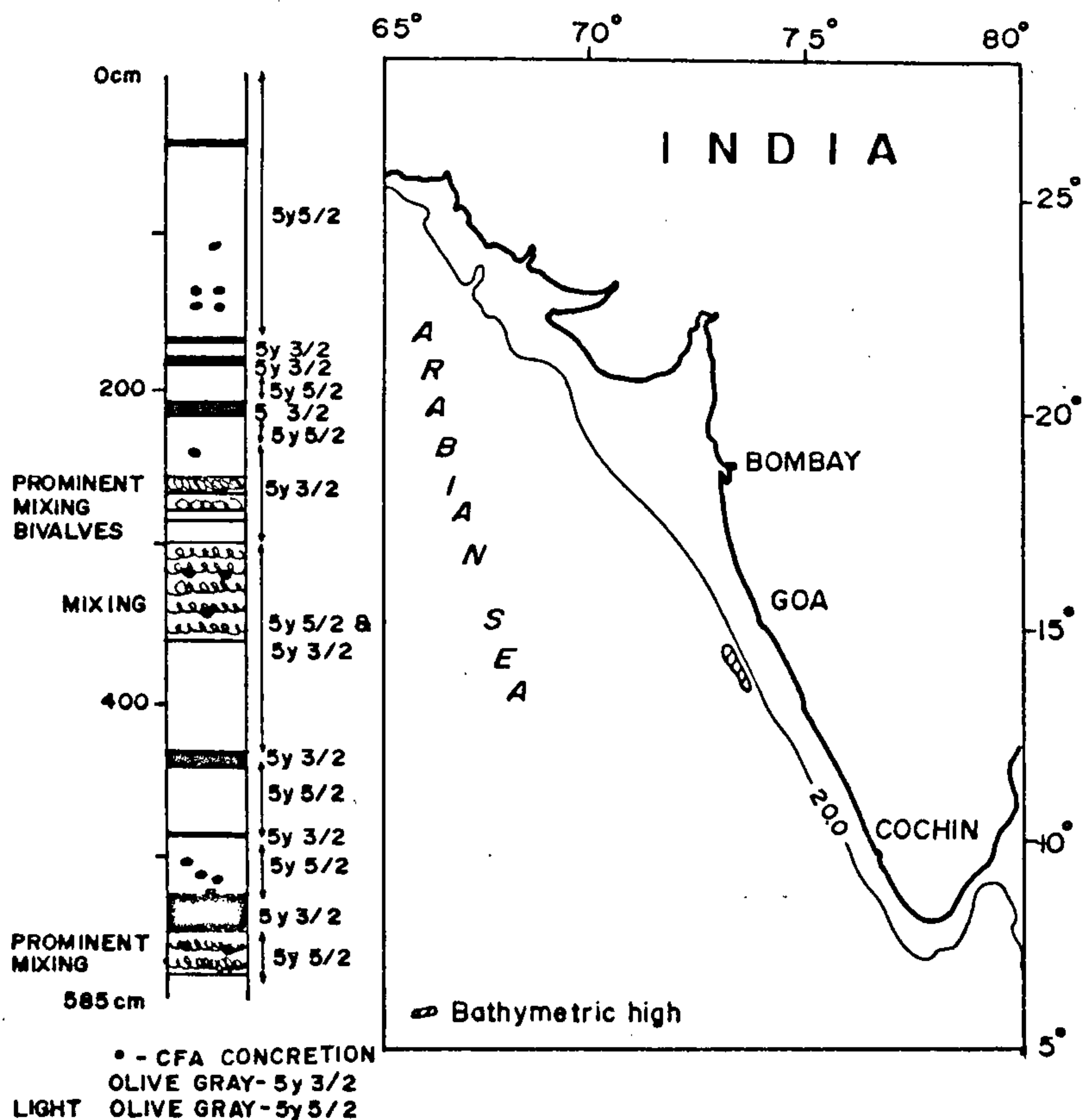


Figure 1. Location of the core and down core lithological variations.

concretions from Numibian shelf have similar P_2O_5 content (av = 32.10%). However, Al_2O_3 (0.03–4.5 wt%) and SiO_2 (0.4–13.52%) in the Namibian concretions are much higher than in those of the present study (Al_2O_3 : <0.1 wt% and SiO_2 : <0.02 wt%). Namibian phosphorites have CFA with admixtures of quartz, mica, feldspars and calcite⁵, whereas the concretions in this study comprise of only CFA (Figure 3).

Marine phosphorites are reported to form mainly due to three processes: (1) Replacement of pre-existing calcareous material; (2) Authigenic/diagenetic precipitation and (3) Microbial mediation. The phosphorites of western shelf of south Africa are suggested to have formed by the replacement of limestones and other calcareous skeletons¹⁵. Marine phosphorites form in the regions of intense upwelling that leads to high biological productivity and supply of organic matter to the underlying sediments is higher resulting in an anoxic environment¹⁶. Decomposition of organic matter in the sediments release phosphate into the interstitial waters which precipitate as CFA¹⁷. However phosphorites are also found

on the shelves of eastern Australia and western south Africa, where bottom sediments are not rich in organic content^{6,18}, implying that phosphogenesis can occur in diverse oceanographic settings. O'Brien *et al.*⁸ suggested that the phosphogenesis off eastern Australia may be bacterially mediated. The role of benthic microbial mats in the formation of phosphatic nodules, crusts and mudstone phosphorites of various geological periods has been reported¹⁹.

The concretions of the present study do not exhibit any replacement rims or precursor structures such as calcareous shells and lithified carbonates. Further, the X-ray diffractograms and SEM observations show neither calcite nor free carbonate minerals, ruling out the possibility of formation related to the replacement process. Therefore, these concretions differ in P_2O_5 content, mineralogy and origin from those of the shelf region.

On the western continental shelf of India, phosphatization of algal nodules was reported to be bacterially mediated as the phosphate grains consist of fungal filaments¹³. The SEM and petrological studies of various

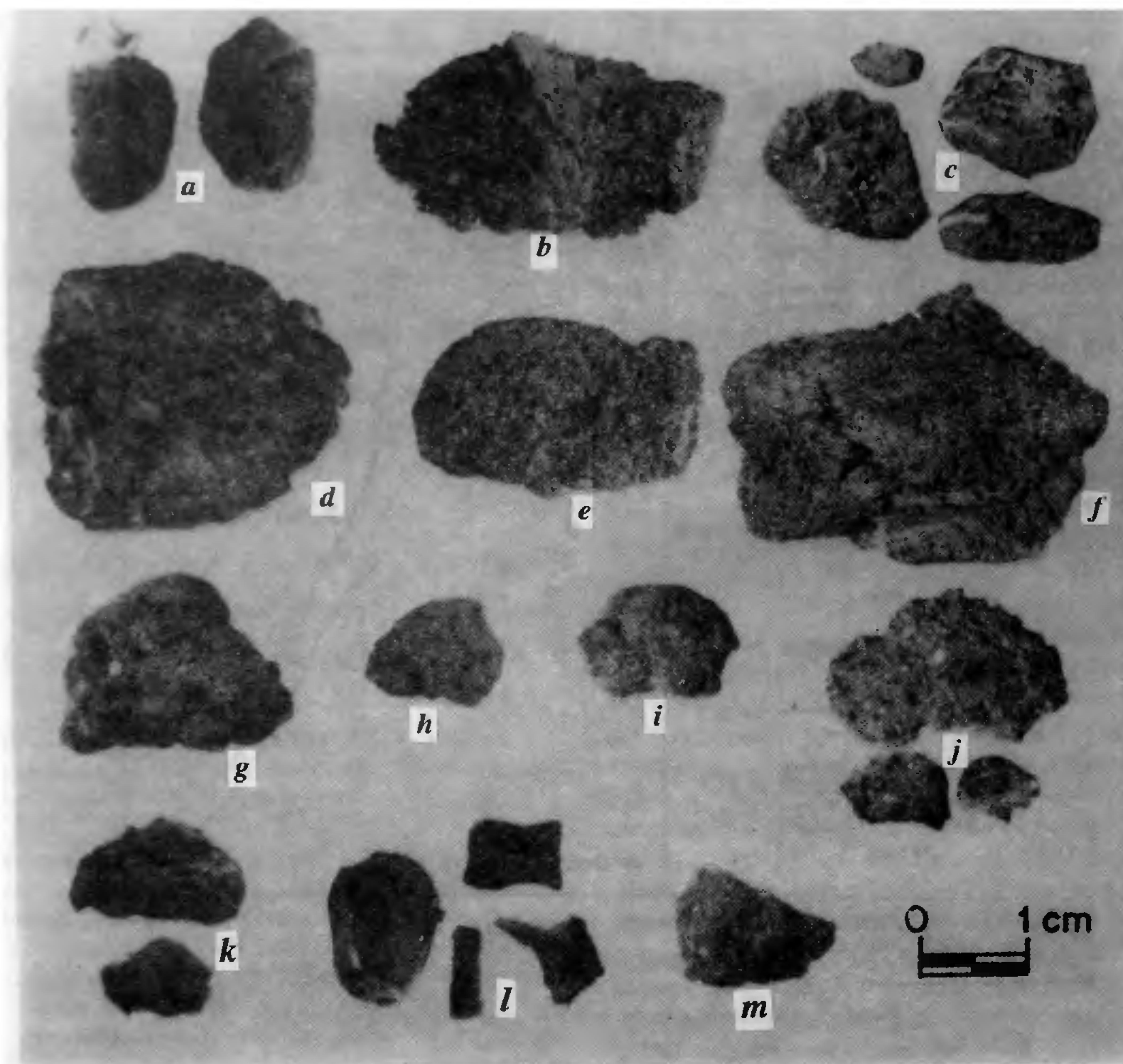


Figure 2. Photographs of concretions recovered from the sediments of the core MH-1.

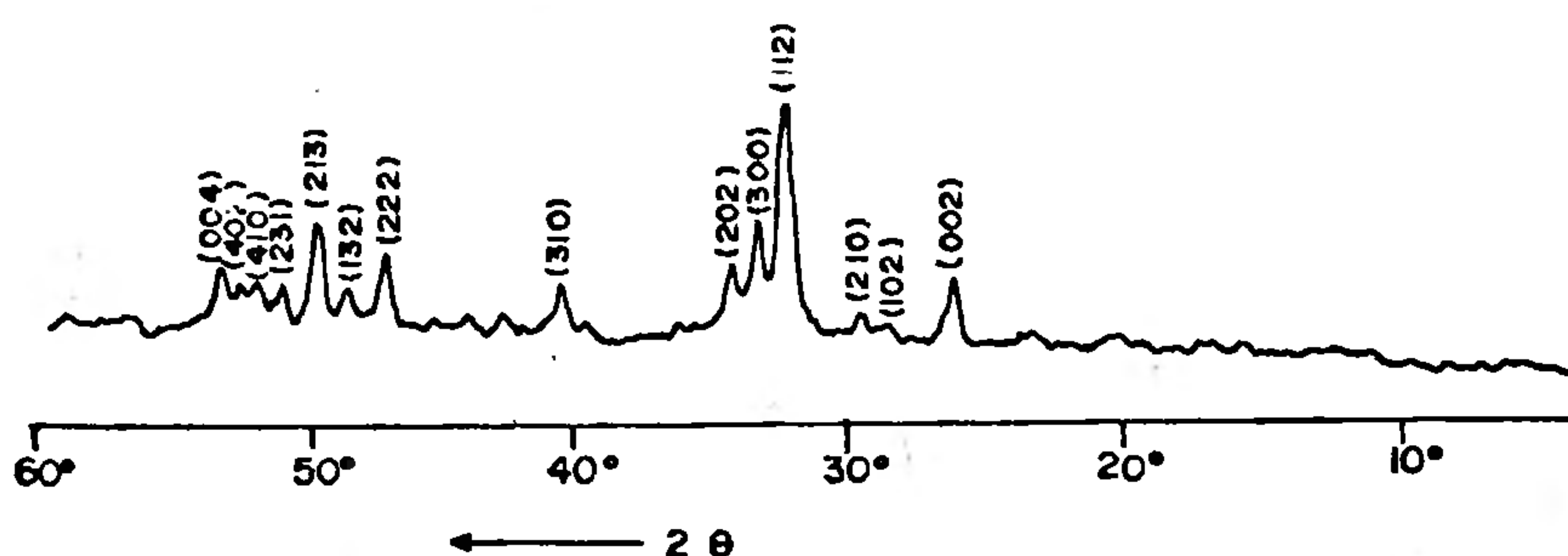


Figure 3. X-ray diffractogram of a phosphorite concretion showing only characteristic CFA reflections.

sections of several concretions in the present study, have not revealed the presence of any bacterial or/and fungal filaments and structures such as globular clusters either in microcavities or as attachments in the concretions.

Therefore, it is unlikely that these concretions are formed due to microbial mediation.

The origin of the phosphorite concretions is suggested to be a result of the diagenetic precipitation of phos-

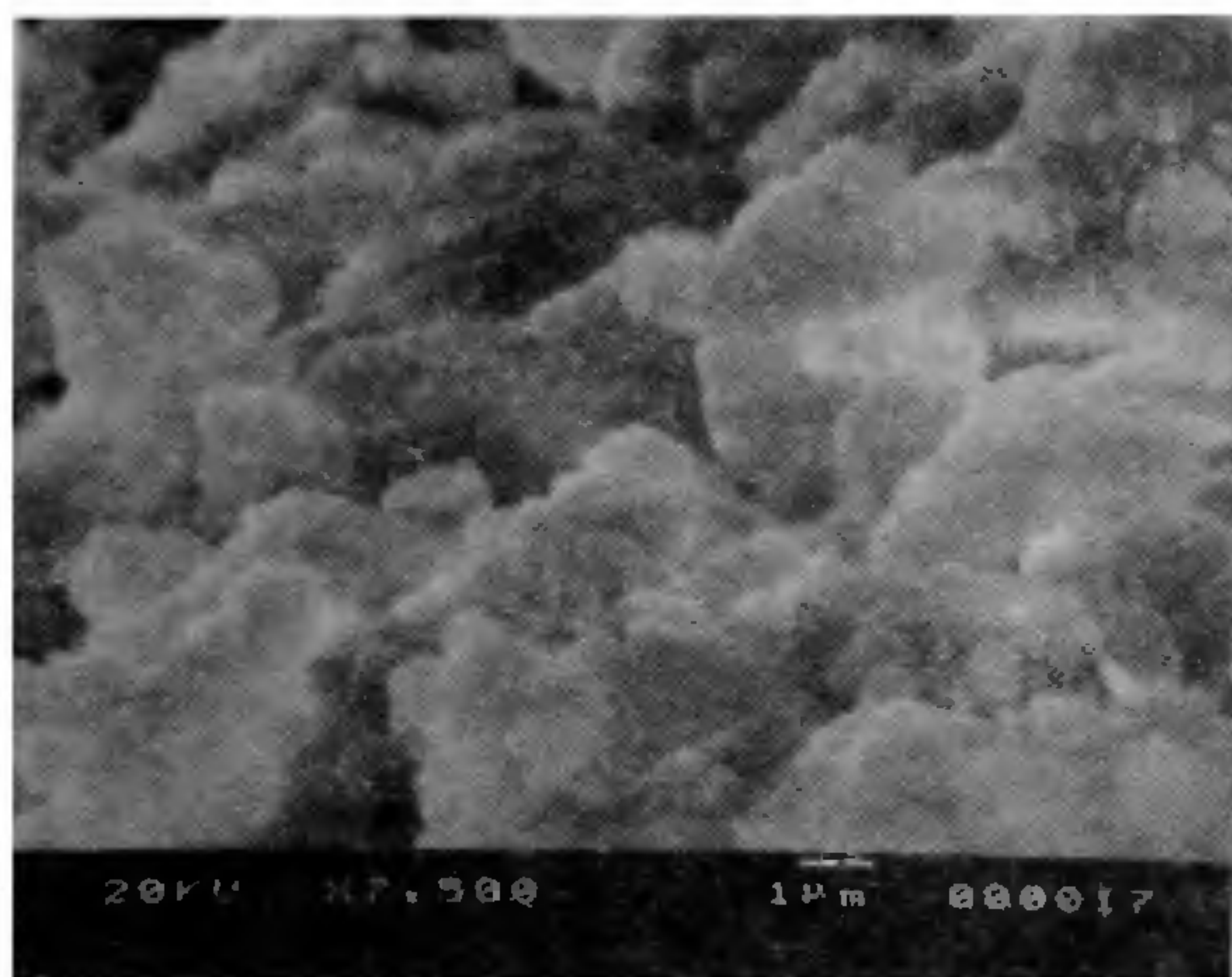


Figure 4. SEM photograph of freshly broken surface of a concretion.

Table 1. Comparison of average P_2O_5 content of offshore phosphorite nodules from various locations with the present study. Figures in parentheses indicate the number of analyses

| Location | Average P_2O_5 wt% content |
|--------------------------------------|--------------------------------------|
| Peru-Chile ³ | 22.61 (15) |
| Namibia ²² | 32.10 (4) |
| Eastern Australia ⁷ | 9.64 (80) |
| Agulhas Bank ¹⁵ | 14.82 (3)* 10.26 (3) [†] |
| Western shelf of India ¹³ | <9.50 |
| Western continental margin of India | 32.75 (6) |
| Present study | |

*Iron poor, [†] Iron rich.

phorus within the sediments. The western continental margin of India experiences intense upwelling during the SW monsoon, leading to high biological productivity in the surface waters, which result in the enhanced supply of organic matter to the seafloor. Further, an intense oxygen-minimum zone intersects the slope of the western continental margin of India between 250 and 1500 m (ref. 20). The core was collected from a water depth of 320 m (within the OMZ) below the upwelling region and the sediments are organic-rich (organic carbon: 0.8 to 2.8 wt%). The sediments deposited on the slope turn anoxic as the rate of consumption of dissolved oxygen in interstitial waters by degradation of organic matter is higher than its replenishment. The presence of pyrite in the core and high uranium content in the sediments (10 ppm) suggest that the environment in the sediments is suboxic to anoxic. Under such oxygen-depleted conditions, bacterial degradation of organic matter releases phosphate into interstitial waters. Further, interstitial water phosphate may also have been derived from the

dissolution of fish debris. The phosphate thus enriched in the interstitial waters is precipitated as microgranular CFA. These microgranular phosphorites were probably consolidated later and progressively became concretions with time. Therefore, the origin of these concretions could be due to the authigenic precipitation from diagenetic fluids.

The concretions are present from 110 cm to the bottom of the core. Their absence in the upper 1 m of the core suggests that these concretions are not modern and phosphogenesis occurred in the past. Flat-topped topographic highs in the mid-slope region experience erosion/winnowing due to internal wave generation²¹ resulting in low sedimentation rates. The sediment samples from different intervals were measured for ^{14}C to obtain sedimentation rate. The activity of ^{14}C could not be detected, implying that these sediments are older than at least 35 ky. To ascertain the age of the concretions, U/Th disequilibrium method was attempted. The ages invariably are in excess of the dating limit of the method (> 250,000 yrs) as the $^{230}Th/^{234}U$ activity ratio is 0.95 ± 0.03 . Further, the $^{234}U/^{238}U$ activity ratio (0.96 ± 0.02) is near secular equilibrium, indicating that their concretions are older than 0.8 m.y. (early Pleistocene).

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Effect of tetraethylammonium ions and 4-aminopyridine on osmotic stability of *Saccharomyces cerevisiae*

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Tetraethylammonium bromide (TEA) and 4-aminopyridine (4-AP) are lethal to *Saccharomyces cerevisiae*. However, the growth of yeast cells is restored on addition of osmotic stabilizers, i.e. 0.2 M KCl, 0.2 M NaCl or 0.4 M mannitol, to the plates containing inhibitory concentration of TEA and 4-AP. 4-AP induces osmotic stability defects instead of blocking K⁺ channels in *S. cerevisiae* as reported in animal cells. As a result, this drug causes cell lysis whereas TEA seems to cause lethality by bringing about some other changes in the plasma membrane of the yeast cells.

ALL organisms require K⁺ ions. In plants and fungi, intracellular K⁺ ions serve a variety of vital functions, including the control of cell shape and turgor pressure¹. In yeast, one of the important functions of K⁺ is suggested to neutralize the negative charge of cellular anions². Like all other organisms, *Saccharomyces cerevisiae* accumulates K⁺ ions from the external medium to fulfil the cellular requirements. The concentration of K⁺ inside the cells may be 10-20 times higher than in the surrounding medium. The transport of K⁺ ions in the cell takes place through various transporters/channels. Various pharmacological drugs including tetraethylammonium bromide (TEA) and 4-aminopyridine (4-AP) have been reported to block K⁺ channels in animal cells^{3,4}. The present study is an attempt to investigate the effects of TEA and 4-AP on K⁺ uptake and viability of *S. cerevisiae*.

Yeast cells were grown on yeast extract, peptone, dextrose (YPD) medium and synthetic complete medium agar plates having different concentrations of TEA and 4-AP. The growth of yeast cells was completely inhibited at 800 mM concentration of TEA and 15 mM concentration of 4-AP on YPD medium agar plates. However, on synthetic complete medium agar plates, the lethal concentration of TEA and 4-AP was 150 and 2 mM, respectively (Table 1). High inhibitory concentration of TEA and 4-AP in YPD medium as compared to synthetic complete medium suggests the presence of high concentration of ions and other molecules (nutrients) in the YPD medium which may be diluting the effect of these drugs. TEA and 4-AP are known to block K⁺ transporters in animal cells^{3,4}. The inhibition of growth of *S. cerevisiae* in the presence of TEA and 4-AP might also be because of blocking of K⁺ transporters in yeast cells.

Further, the growth of *S. cerevisiae* on synthetic complete medium agar plates, containing inhibitory

Table 1. Effect of TEA and 4-AP on viability of *S. cerevisiae* on YPD medium and synthetic complete medium agar plates

| Medium used | Drug | Concentration of drug (mM) | Viability (%) |
|---------------------------|------|----------------------------|---------------|
| YPD medium | TEA | 100 | 100 ± 1.16 |
| | | 200 | 100 ± 2.64 |
| | | 400 | 68 ± 6.51 |
| | | 600 | 64 ± 5.86 |
| | | 800 | 0 |
| | 4-AP | 2.5 | 100 ± 3.51 |
| | | 5 | 100 ± 2.52 |
| | | 10 | 75 ± 6.03 |
| | | 15 | 0 |
| | | | |
| Synthetic complete medium | TEA | 50 | 100 ± 6.43 |
| | | 100 | 100 ± 4.04 |
| | | 150 | 0 |
| | | 200 | 0 |
| | | | |
| | 4-AP | 0.25 | 100 ± 4.72 |
| | | 0.50 | 100 ± 5.01 |
| | | 1 | 50 ± 3.05 |
| | | 2 | 0 |
| | | | |

Results are mean ± SD of three independent experiments.

Table 2. Effect of KCl, NaCl and mannitol on the growth of *S. cerevisiae* on synthetic complete medium agar plates containing TEA and 4-AP

| Drug | Concentration of drug (mM) | Per cent viability | | |
|------|----------------------------|--------------------|--------------|------------------|
| | | KCl (0.2 M) | NaCl (0.2 M) | Mannitol (0.4 M) |
| TEA | 100 | 100* | 100* | 100 ± 2.52* |
| | 150 | 100 | 100 | 100 ± 2.08 |
| | 200 | 0 | 0 | 0 |
| 4-AP | 1 | 100 | 100 | 100 ± 4.58 |
| | 2 | 100 | 100 | 100 ± 2.00 |

Results are mean ± SD of three independent experiments.

*Early appearance of colonies.