

HOLOCENE PHOSPHORITES OF THE WESTERN CONTINENTAL MARGIN OF INDIA

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ABSTRACT

Seventeen samples collected during different cruises of *RV Gaveshani*, were analysed by X-Ray diffractometer for apatite. These samples consists of algal and oolitic limestones and were recovered from depths ranging from 70 to 150 m on the western continental shelf from Saurashtra to Kerala. Prominant apatite peak was present only in the algal limestones off Goa. These occur as nodules and are similar in appearance to rhodoliths. Minerals present, in order of abundance, are high-magnesium calcite, francolite (carbonate fluorapatite), quartz, feldspar and aragonite. P_2O_5 concentration varies between 0.8% and 10.8% indicating a wide variation in chemical composition with the area. Age determined by the radiocarbon method is 11,040 years. It appears that these phosphorites were formed by diagenesis and the enrichment of phosphate in these limestones might be related to the physico-chemical activity of microorganism that built the algal mat.

Key-words: Phosphorites, Continental shelf, relict, India.

INTRODUCTION

During the course of a review of the prospects of offshore mining in India, Qasim and Nair (1978) had indicated the possibility of the occurrence of phosphorite on certain parts of the western continental shelf of India. The inference on the possible presence of phosphorites was based on the fact that phosphatised ooids (Nair, 1969) and phosphate in the sediments (0.8 to 1.2 per cent P_2O_5 , Rao, Rajamanickam, Paropkari and Murty, 1978) are present on the western shelf. The phosphate enrichment in the sediments may have resulted as a consequence of upwelling taking place on the west facing continental shelf of India. The association between phosphorite and upwelling has been extensively documented (Baturin, 1982; Kolodny, 1981 and reference therein) (Fig. 1) and classic examples of modern phosphorite formation associated with upwelling regions are Chile/Peru (Burnett, 1980) and southwest Africa (Bremner, 1980). The object of this paper is to present preliminary data on the presence of phosphate rich limestones (phosphorites) on the western shelf of India.

MATERIALS AND METHODS

Rocks obtained by dredging during the various cruises of *RV Gaveshani* were the samples that were examined. Invariably the samples were limestones of various kinds and these occur as outcrops on the outer continental shelf from Saurashtra to Kerala. These were washed in tap water, dried and ground approximately to -230 mesh. The powdered samples were packed in the aluminium sample holder and analysed on a Philips X-ray diffractometer

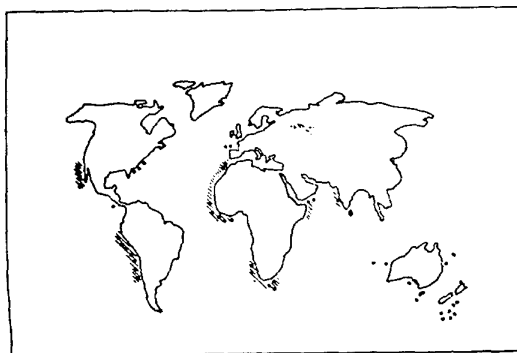


Fig. 1. Map showing the location of marine phosphorites (black dots) and regions of upwelling (hatched areas) in different regions of the world.

using nickel filtered $\text{Cu K}\alpha$ radiation. All the samples were initially scanned from 25° to 35° at $2^\circ 20/\text{min}$. Where a prominent peak of the principal reflection of apatite ($32^\circ 2\theta$) was observed, the samples were treated with 0.5N acetic acid to remove the carbonates and rescanned from 25° to 54° at $1^\circ 20/\text{min}$. to obtain a detailed diffractogram. Selected samples were analysed by colorimetric method in duplicate to determine the P_2O_5 content in the acid soluble fraction. Table I shows the salient characteristics of the western Indian phosphorites in comparison with the Chile/Peru and Namibian phosphorites. Also included in the table are data on onshore phosphorites of India.

SEDIMENTARY FRAME WORK OF WESTERN SHELF

The sediment of the western shelf consists of basically two distinct sediment types. They are the modern organic rich muds which are present to a water depth of 50 to 60 m and the deeper water relict calcareous sands of the outer continental shelf. Radiocarbon age of the sediments and rocks from this relict zone is between 9,000 and 12,000 yrs. One characteristic feature of this outer shelf is the extensive development of a system of ridges of 1 to 5 m in height. These ridges are constituted of algal and oolitic limestones, the former being aerially more extensive (Nair and Hashimi, 1980). The samples examined in the present study are derived from this outershelf ridge zone. Much of this zone is beyond the reach of present day mud deposition.

The hydrographic features relevant to the present study are the prevalence of upwelling and oxygen depleted waters on the continental margin (Fig. 2). The upwelling is seasonal being most prominent during the southwest monsoon season and the associated $\text{PO}_4\text{-P}$ is found in excess of $2\mu\text{g}$ at/litre in the bottom waters (Rao, Rajamanickam, Paropkari and Murty, 1978). An

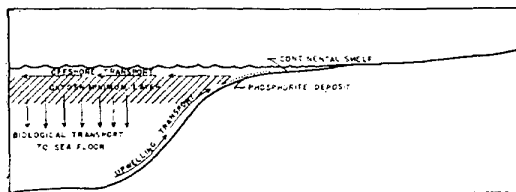


Fig. 2. Relation between coastal upwelling, oxygen minimum layer and phosphorite deposition.

oxygen minimum zone is found at water depths greater than 200 m (Stackelberg, 1972). Occasional incursion of this oxygen minimum waters are reported on the shelf but over most of the time the shelf waters are considered to be well oxygenated. The primary productivity of the shelf waters is generally high and is of the order of 0.5 to 1 g C/m²/day.

RESULTS AND DISCUSSION

The samples bearing the phosphate are greyish coloured nodules with black encrustations and occur in water depths of 70 to 150 m (Fig. 3). They range in diameter from 5 to 10 cms. They are irregular in shape and have lumps and protuberances. Polished nodules exhibit distinct bandings and laminations and suggest that they originate from calcareous algae. They are thus similar in appearance to rhodoliths. Out of the 17 samples analysed, 4 samples (Fig. 3) exhibit the distinct $32^{\circ} 2\theta$ reflection of the apatite mineral. The apatite occurs as greyish black film and crust on the surface of the samples. No apatite was observed in the oolitic limestones. The most prominent reflection was seen in the samples 775 and 748. Calcite is the dominant mineral in the whole sample. In keeping with the coralline nature of the rock the calcite is the high-magnesium variety, its peak occurring at $29.9^{\circ} 2\theta$. Aragonite is either present in small quantities or absent.

The carbonate free X-ray diffractogram of sample No. 775 is shown in Fig. 4. The principal mineral present is carbonate fluorapatite (francolite) and the other minerals present in minor amounts are feldspar and quartz. The diffractogram shows sharply defined peaks indicating that the francolite occurs as well crystallised mineral. The structural CO₂ content determined by the Gulbrandsen's (1970) peak pair method yielded a value of 4.47 weight per cent. Francolite has the general formula Ca₅(PO₄)₃(F.OH) and it forms the main mineral of recent and ancient phosphorites. The maximum P₂O₅ content in the acid soluble fraction of the nodules was 10.8 and the minimum was 0.8% indicating wide variation in chemical composition within the area. X-ray analysis of the insoluble residue of the nodules shows the presence of montmorillonite, illite, kaolinite and chlorite.

Age determination carried out on these phosphorites gave an age of $11,040 \pm 410$ years. It is similar in age to other radiocarbon dated limestones -390 north and south of the nodule location. These dates are on ooid grains, oolitic

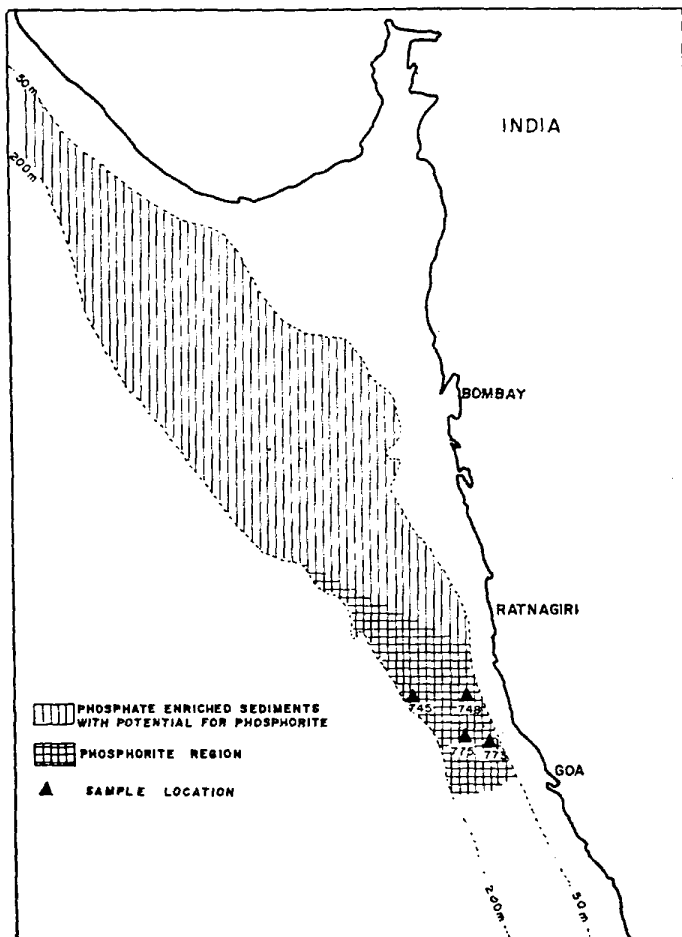


Fig. 3. Map showing the location where phosphorite has been obtained by dredging.

limestones, algal limestones and composite shells (Nair and Hashimi, 1980). All the dates were determined on samples which were treated with dilute HCl to remove encrusting and infilled modern carbonates, and are reported with respect to a half life of 5730 years.

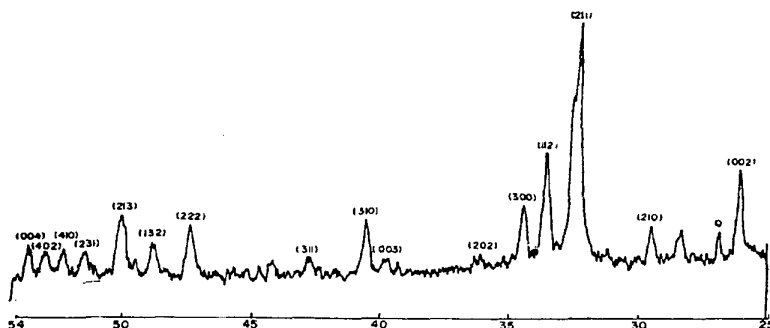


Fig. 4. X-ray diffractogram of the carbonate free phosphorite.

The only other two areas where Holocene phosphorites are forming are on the continental margins of Chile and southwest Africa. Table I compares the phosphorites reported in the present study with those of the former. Principal differences between them are in the nature of the host rock but similarities are present in chemical composition, age of the samples and mineralogy.

The two principal mechanisms that account for the origin of the marine phosphorites are diagenetic and authigenic. Diagenetic processes involve the replacement of the carbonate ion with phosphate and other ions or interstitial precipitation of apatite, whereas authigenic phosphorites result from direct precipitation from sea water. Recent review of the problem by Kolodny (1981), for example, suggests that a given deposit may result from one or both processes but acting at different times.

Table I. Comparison of modern and ancient (land) phosphorites.

Location	P ₂ O ₅ %	Age	Mineral Phase	Host rock	Source
Off Namibia (S.W. Africa)	8-32	Holocene	Flourapatite	Diatomaceous mud	Bremmer, 1980
Off Peru	15-25	Pleistocene	Apatite	Pellets	Burnett, 1980
Off Western India	0.8-11 (acid soluble fraction)	Holocene	Francolite	Algal nodules	This Report
Onshore Phosphorite-India					
a) Rajasthan	15-36	Precambrian	Apatite and Hydroxyapatite	Stromatolites	Deb, 1980
b) Mussoorie	6-35	Permo-Trias	Flourapatite and carbonate apatite	Chert and shale	Deb, 1980

It would be premature at this stage with our limited data to comment on the origin of phosphorites of the western Indian margin. But a speculative conjecture would be that because the apatite occurs only in the algal nodules and not in the associated limestones, the process might be diagenetic. It should be emphasised here that even though phosphate was detected in the ooids (Nair, 1969) by chemical analysis, no apatite was recorded when the same ooid grains were analysed by X-ray diffraction. The reason being that the apatite content in the ooids are below the detection limit (5%) of the X-ray diffraction method. On the other hand the algal nodules consistently showed the presence of well crystallised apatite by the same method. Since the algal nodules (rhodoliths) are spheroidal forms of algal stromatolitic structures formed by crustose coralline algae in high energy environment (Adey and Mac Intyre, 1973), it is possible that the precipitation of phosphate might be controlled by the physico-chemical activity of the micro-organisms that built the algal mat. Since these nodules are 11,040 years old, the physico-chemical conditions prevailing at that time, in particular associated with the low stand of sea level, about 100 m below the present (Nair and Hashimi, 1980), might be the determining factors rather than the conditions now present.

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