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The occurrence of phosphorites on the Calicut mount, off Kerala, Lakshadweep Sea, India

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A highly altered carbonate rock was recovered from the mount, off Calicut, Kerala. Bulk chemical analysis of the rock showed that it contains ~ 21 % P_2O_5. The rock consists of fine to coarse lithic and bio-clasts embedded in brown to the yellow coloured phosphatic matrix. Detailed SEM-EDS of the rock piece indicates micro-globular and nodular growth of phosphorite around calcite to form a core-rim structure, with P_2O_5 as high as 31.67 weight percentage. The X-ray elemental mapping carried out using EPMA indicates highest P_2O_5 (29.87 %) on the altered surfaces. Microstructural and geochemical analyses suggest authigenic/diagenetic precipitation of phosphorite on the carbonate rock.

[**Keywords**: Authigenic precipitation, Calicut mount, Carbonate fluorapatite, Phosphorite]

Introduction

India's economy depends largely on agriculture and a vast amount of fertilizers are needed for enhanced crop production. Phosphorite is one of the major minerals required for the fertilizer industry. Domestic production of rock phosphate in India is about 2.1 million tonnes against the demand of 10 million tonnes[1]. To bridge the deficit of supply against the demand, India imports high-grade rock phosphate from Morocco and Jordan. With no suitable substitute for phosphate in the fertilizer industry; the country is searching for phosphate from alternate indigenous sources. Several workers have reported the sporadic occurrences of phosphorite in the Indian Exclusive Economic Zone (EEZ)[2-10]. The Geological Survey of India has brought to light the occurrence and geological control of phosphogenesis off west coast of India by conducting several exploration cruises for marine minerals[11-14]. The reported occurrence from the Indian margin are phosphatised oolites on the continental shelf edge in relict calcareous sand facies[3], concretions in bathymetric high off Goa on western continental margin[4] and solid-phase phosphorus and benthic phosphate fluxes in continental slope of Arabian Sea sediments[15]. Besides, phosphatised sediments[16] and phosphatized algal limestone[17] were recovered from the continental margin off Chennai and Goa, respectively. Open-ocean phosphorites occur on isolated seamounts, plateaus, ridges, and other elevated areas of the seafloor[18]. Phosphatic nodules comprise of bioclasts and bone fragments were reported from Murray Ridge, NW Arabian Sea[19]. Radiometric ages of phosphorites from the west coast of India range between 5.8 – 13.9 k.y[20]. This paper reports the occurrence of high-grade phosphorite from a seamount off Calicut, west coast of India.

The Geological Survey of India has carried out preliminary exploration onboard *O. R. V. Samudra Ratnakar* for phosphorite in the seamount off Calicut (Calicut mount) and Elikalpeni bank, in Lakshadweep Sea. The Calicut mount and Elikalpeni bank are the two detached mounts rising from the seafloor from about 1800 m water depth. The flat summit of the Calicut mount is as shallow as 20 m water depth, with summit area of 93 km^2. The summit depth of the Elikalpeni bank is much shallower at 12 m water depth with a summit area of 37 km^2 (Fig. 1). The base of the Calicut mount and Elikalpen bank covers an area of 248 km^2 and 129 km^2, respectively. Relict and live corals, shell fragments and calcareous debris cover the summit and upper slope of both the mounts. Terrigenous sediments cover the lower slope of the seamount from 300 to 900 m water depth and seafloor surrounding the seamounts.

Materials and Methods

A total of 45 sediment samples were collected from the terraces identified on the flanks of Calicut mount and Elikalpeni bank, using Van Veen and Okean grab samplers. A rock fragment was recovered in one of the grab samples collected from 666 m water depth on the south-western flank of the Calicut mount. The onboard phosphate test conducted on the rock with ammonium venadomolybdnate solution inferred the presence of concentrated phosphate in the rock fragment. Detailed studies have been carried out to confirm the phosphate enrichments and to understand the mechanism of phosphorite formation. The recovered pieces were hard and irregular with greenish to a black coating on the pitted surface (Figs. 2A – C). The freshly broken surfaces of the rock yielded white coloured phases. Fresh and weathered portions of the samples were studied separately to locate the phosphate enrichment.

The phosphate content of the rock pieces was determined in the lab by the colourimetric method after treating with ammonium venadomolybdate

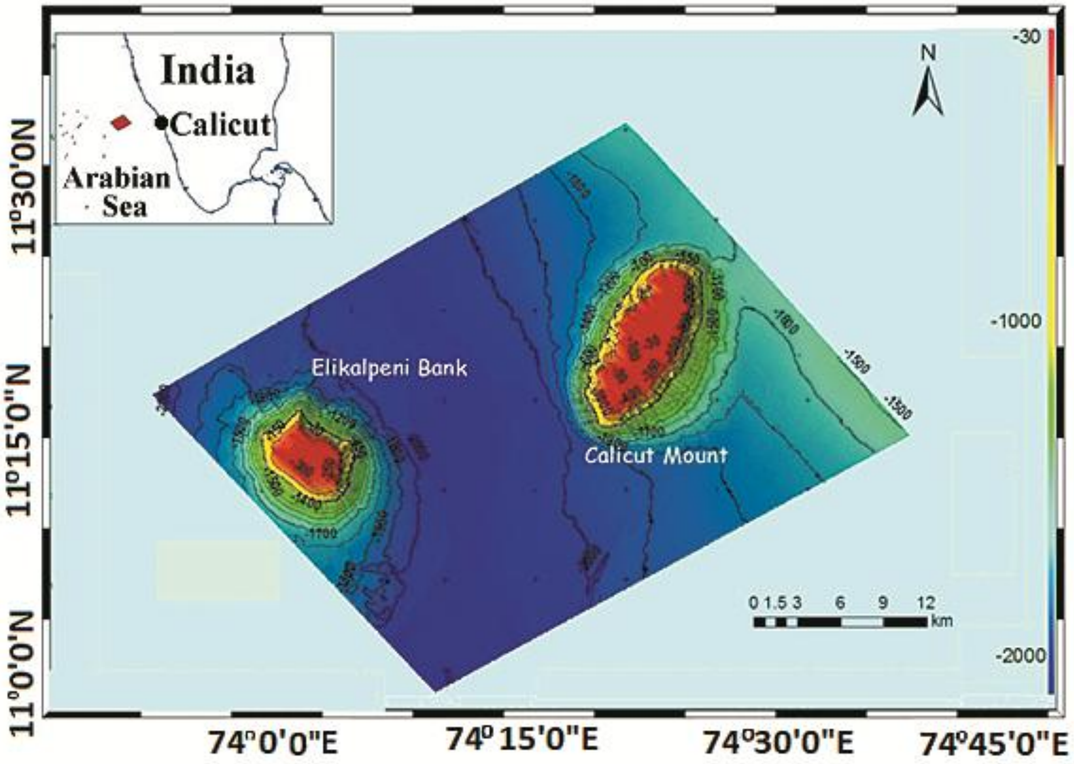

Fig. 1 — Locations of Calicut mount and Elikalpeni bank, off Calicut, Kerala

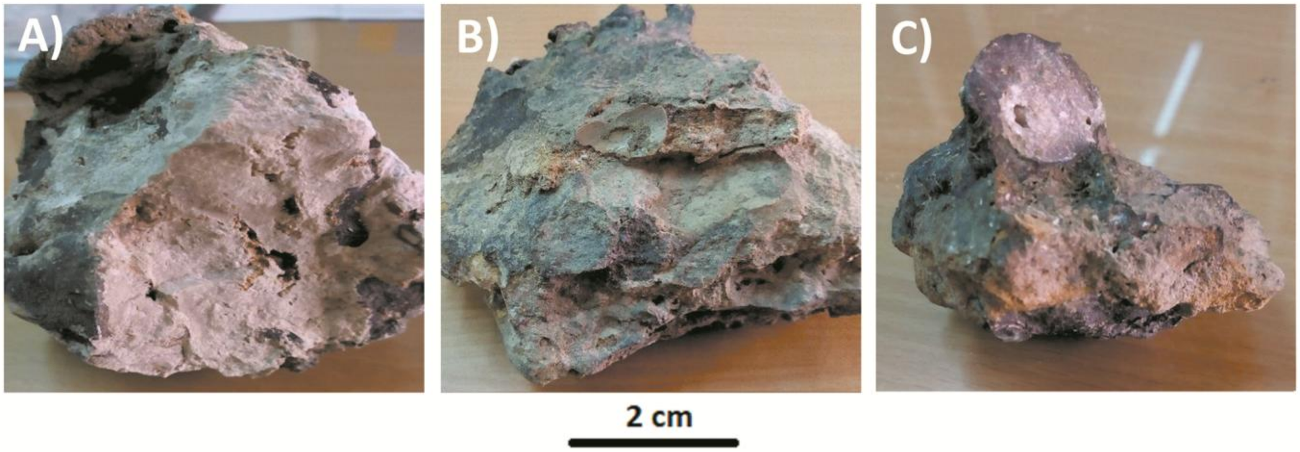

Fig. 2 — (A) Photograph of sample G-34A, white coloured piece of phosphatic rock with disseminated black spots; (B) Sample G-34B-Altered, dull, off-white piece of phosphatic rock with impregnations of shells and hard black encrustations; and (C) Sample G-34C- Black coloured, hard phosphatic rock piece

reagent with the help of a spectrophotometer[21]. The samples were oven-dried and powdered. These powdered samples were digested with aquaregia and hydrofluoric acid following the standard digestion procedures for determining major and trace elements on Flame-AAS. The samples were digested on a hot plate using HF-$HClO_4$ -HNO_3 triple acid mixture and analyzed on Varian 820 MSICP-MS for determining Rare Earth Elements (REE).

The rock samples indicating high P_2O_5 content were selected for the Scanning Electron Microscopic (SEM) analysis. Freshly broken surfaces of the rock and pieces of substrates were glued on to the stubs, coated with gold and examined under VEGA3 (TSCAN make) Scanning Electron Microscope at SEM Lab, GSI Regional Office, Hyderabad. Three to four parts of rock from each zone were mapped under SEM.

For Electron Probe Micro Analyzer (EPMA) studies, 50 μm thick polished thin sections were prepared in such a way that both the altered, fragile part, as well as the compact, white, carbonate parts are exposed. These sections were studied at NCPOR, Goa on CAMECA SX Electron Probe Micro Analyser. Finely polished thin sections were coated with carbon for better conductivity. Micro-spot, as well as profile analyses, were carried out at an accelerating voltage of 15 kV and probe current of 20 nA. Beam diameter of 5 – 30 μm was applied for the analysis and the semi-quantitative weight percentages of P_2O_5, TiO_2, SiO_2, Al_2O_3, FeO, CaO, MgO, K_2O, Na_2O, F, Cl, and SO_2 were obtained. X-ray maps were prepared for the element P with the same instrument.

Results and Discussion

Thin section studies of sample G-34C under a polarising microscope showed a brown to a yellow coloured fine-grained matrix in the sample (Fig. 3A), with bioclasts and a few lithic fragments in the phosphatic portion of the rock. The lithic clasts are fine to coarser particles in sub-rounded, angular or irregular shapes (Fig. 3A). Bioclasts observed are remains of bones, scales, and teeth of the organisms. SEM-EDX studies indicated calcite and phosphatic composition of the matrix.

The rock samples collected at locations G-13 and G-34 yielded 16.5 and 21.3 % P_2O_5, respectively (Fig. 4). Three sub-samples generated from the single big chunk of G-34 were again analyzed for bulk P_2O_5 content (Figs. 2A – C). Sample 34A (Fig. 2A), white coloured massive rock with disseminated black spots contained 4 % P_2O_5. Sample 34B (Fig. 2B), altered rock piece of dull off-white colour with impregnations of shell fragments and black encrustations had 15 % P_2O_5. Sample G-34C (Fig. 2C), pitch-black, hard, nodular, rock piece contained 10 % P_2O_5. Therefore, petrographic studies of the samples G-34B and G-34C were carried out to understand the nature of P_2O_5 enrichment in those samples.

The weathered part of the rock sample show high P_2O_5 and SiO_2 contents, lower $CaCO_3$ as compared to the unweathered part of the rock suggesting the alteration of the fresh lime rock might have facilitated the enrichment of P_2O_5. The shale-normalised REE plots of phosphorite-bearing rock show HREE-enriched pattern with negative Ce anomaly[22] (Figs. 5 & 6). The enrichment of HREE is a well-established fact in many phosphorites[23].

SEM-EDX studies carried out on the fragments G-34A, B, andC also showed high P_2O_5 content in

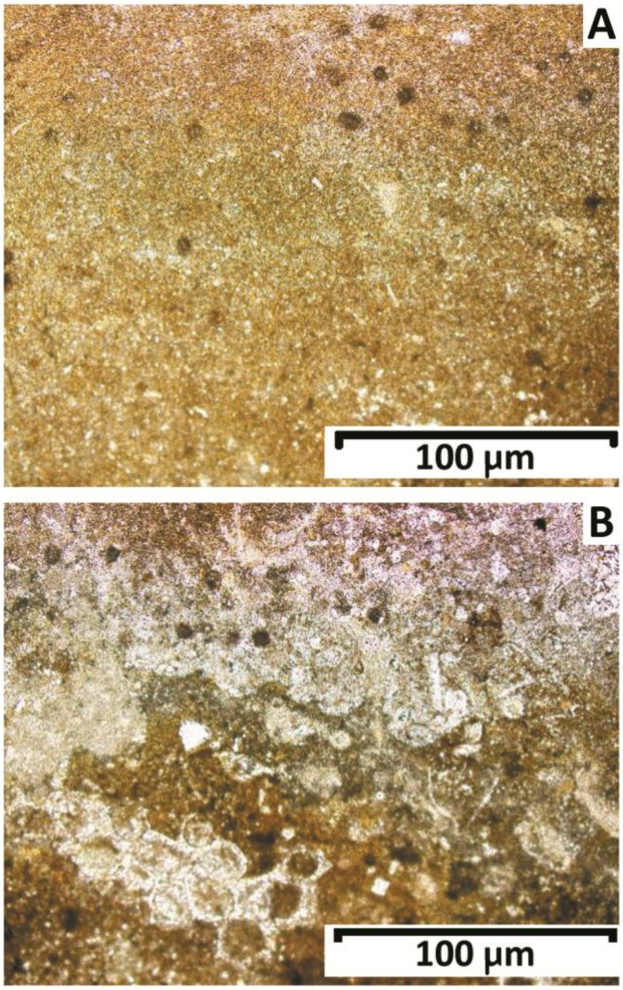

Fig. 3 — Thin section of the phosphorite sample depicting fine grained matrix (A), and bioclasts (B)

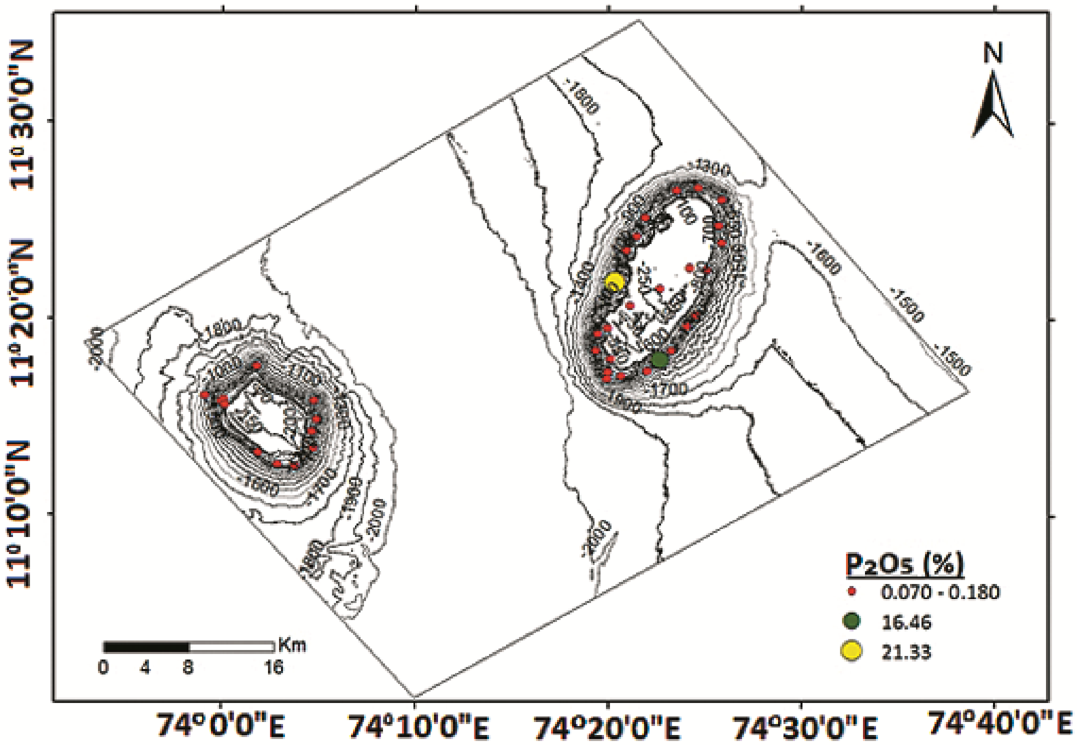

Fig. 4 — Distribution of P_2O_5 in sediments and rock samples collected from the two seamounts off Calicut, Kerala

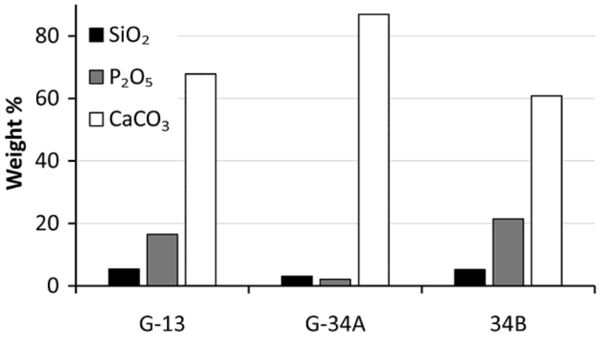

Fig. 5 — SiO_2, P_2O_5 and $CaCO_3$ concentration in rock samples

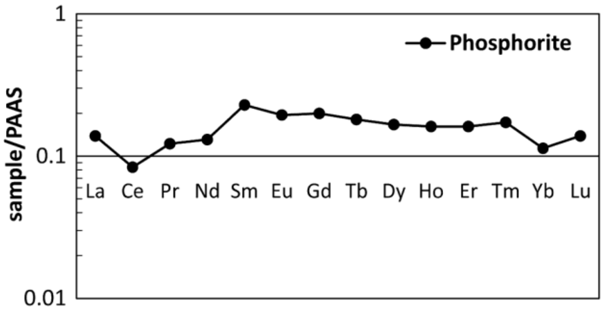

Fig. 6 — REE normalised plot of the phosphorite rock G-34

the samples. The studies also delineated phosphatic mineral phases and the variation in chemical composition at different zones. Fragments from G-34C are mainly made up of calcite and phosphorite (Figs. 7A & B). The phosphatic zones are distinctly developed even though it is amalgamated in many places. The phosphate occurs as micro-globules surrounding the calcite crystals, making a core-rim structure with a sharp boundary (Fig. 7D). Well-developed crystals of carbonate fluorapatite were not seen. Presence of pyrite confirms the reducing condition (Fig. 7F).

Fragments separated from G-34B (Figs. 7A – F) are essentially made up of carbonate and phosphorite. There is no well-developed phosphatic zone; compositionally it is made up of Ca, P, Na, Al, S, Mg, Si, and Fe. The SEM results indicated that the phosphatic matrix is a cryptocrystalline/amorphous fluorapatite that forms a nodular structure similar to calcified nanospheres reported from phosphorites of Murray ridge[19]. The SEM-EDX analysis (semi-quantitative) on a phosphatic portion of the rock indicated high P_2O_5 content ranging from 21 to 31.54 wt % (Table 1). SEM-EDX analysis confirms that the phosphorite is mostly made up of P, Ca, Na, F, S, and Mg. Fragments from G-34A are composed entirely of $CaCO_3$ without much variation in chemical composition.

The bulk chemical analyses (21.3 % P_2O_5), as well as SEM studies (21 – 31.5 % P_2O_5), indicate enrichment of P_2O_5 within the rock. EPMA study has

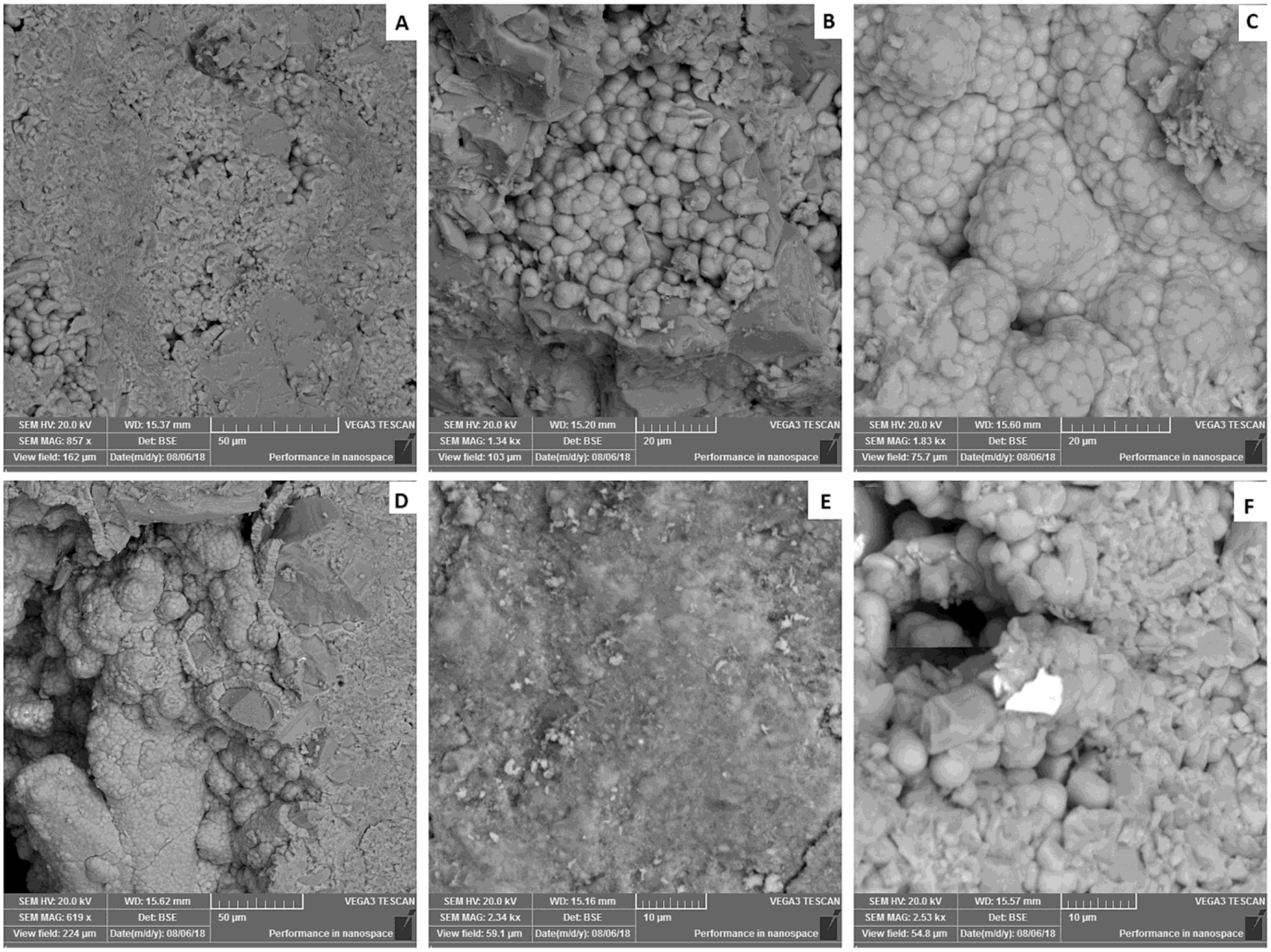

Fig. 7 — SEM images of the selected segments from the phosphorite rock: (A) nodular phosphorite in carbonate matrix, (B) development of nodular phosphorite, (C) botryoidal phosphorite, (D) development of phosphorite around calcite crystals, (E) cryptocrystalline phosphorite, and (F) pyrite along with phosphorite

Table 1 — SEM analysis of Phosphorite-bearing rock (G-34)

Points	Na_2O	P_2O_5	Al_2O_3	SiO_2	FeO	MgO	CaO
G34B1/23	3.01	30.40	2.02	3.14	1.48	2.11	51.88
G34B1/22	1.05	24.88	1.10	9.17	6.23	1.75	51.18
G34B1/25	2.81	27.25	3.04	6.30	3.4	2.3	50.66
G34B1/27	3.02	31.67	0.76	0.9	0.86	1.57	54.22
G34B1/28	2.05	26.11	1.79	2.92	3.03	1.91	57.80

been carried out to understand the chemical composition of the phosphate-bearing parts of the rock in detail.

Chemical composition obtained from EPMA point analysis (Table 2) of G-34 sample showed a P_2O_5 content ranging from 18.09 to 29.87 %, F content between 1.3 and 3.12 wt % and CaO from 31.75 to 51.44 %. X-ray mapping was carried out to find out the variation of P, Ca and Fe content across the layers (Layer A and Layer B) identified in thin sections. Backscattered image (Fig. 8) shows the area selected for X-ray mapping covering both the layers. X-ray maps and profiles for the element P are shown in Figure 9. X-ray mapping for P shows the maximum signal in the phosphatic layer (A) and the signals were very feeble in layer B (Fig. 9C). The X-ray spectrum taken on a profile across the layer from B to A (Fig. 7B) shows the very low count for Phosphorus in layer B, whereas the counts for P increases exponentially in layer A indicating an abrupt change in mineralogy as a result of phosphatic mineral growth on the carbonate surface.

The bulk chemical analysis, SEM and EPMA studies support the enrichment of phosphate in the weathered parts of the carbonate rock. In general, three processes have been suggested for the genesis of marine phosphorites: (1) Replacement of the pre-existing calcareous material, (2) diagenetic/authigenic

Table 2 — EPMA data of phosphorite-bearing rock (G-34)

Points	F	Cl	Na_2O	K_2O	MgO	CaO	FeO	Al_2O_3	SiO_2	SO_2	TiO_2	P_2O_5
11 / 1	1.92	0.05	0.45	0.07	0.83	49.23	0.29	0.03	0.26	0.79	0	18.52
12 / 1	1.3	0.08	0.35	0.12	1.06	45.5	0.98	1.23	2.89	1.23	0.03	26.55
13 / 1	2.37	0.06	0.36	1.47	0.99	31.73	1.13	7.38	24.71	0.95	0.05	20.73
15 / 1	2.11	0.08	0.86	0.53	1.16	43.47	1.12	2.46	5.73	1.18	0.09	26.65
17 / 1	2.34	0.09	1.47	0.28	1.04	40.91	0.87	3.32	11.37	1.19	0.18	25.22
18 / 1	2.43	0.09	0.93	0.27	1.21	45.77	1.05	1.64	3.81	1.12	0.07	26.2
19 / 1	3.14	0.1	0.83	0.24	1.12	44.83	0.9	1.41	3.07	1.37	0.06	28.69
20 / 1	2.49	0.09	0.75	0.24	1.19	42.84	0.85	1.35	2.89	1.26	0.12	28.16
21 / 1	2.95	0.07	0.9	0.25	1.13	45.62	0.91	1.77	3.78	1.3	0.06	27.99
22 / 1	2.8	0.03	0.83	0.21	1.2	46.49	1.12	1.51	2.95	1.24	0.05	27.96
23 / 1	2.66	0.1	0.76	0.15	1.19	45.67	0.87	1.14	2.58	1.36	0.07	28.29
24 / 1	2.54	0.08	0.86	0.28	1.26	45.48	1.25	1.6	3.27	1.2	0.11	26.91
25 / 1	2.71	0.12	0.91	0.33	1.18	43.87	1.02	1.74	3.65	1.26	0.1	27.24
26 / 1	3.04	0.1	0.5	0.19	0.99	38.78	1.02	4.16	13.45	1.47	0.1	29.87
27 / 1	1.51	0.04	0.89	0.16	1.02	39.18	0.67	1.57	3.83	0.95	0.3	22.86
28 / 1	2.29	0.1	0.67	0.23	1.03	42.68	0.84	2.3	4.4	1.1	0.08	25.55
39 / 1	1.64	0.12	0.22	0.12	0.41	43.79	0.88	0.92	2.04	1.04	0.01	28.65
47 / 1	1.85	0.05	0.65	0.1	0.81	48.38	0.65	0.07	0.41	1.22	-0.01	19.95
48 / 1	1.64	0.02	0.57	0.09	0.97	51.44	0.36	0.06	0.38	0.8	0	18.87
49 / 1	1.69	0.03	0.64	0.09	0.95	49.68	0.41	0.07	0.51	0.75	0.01	18.09

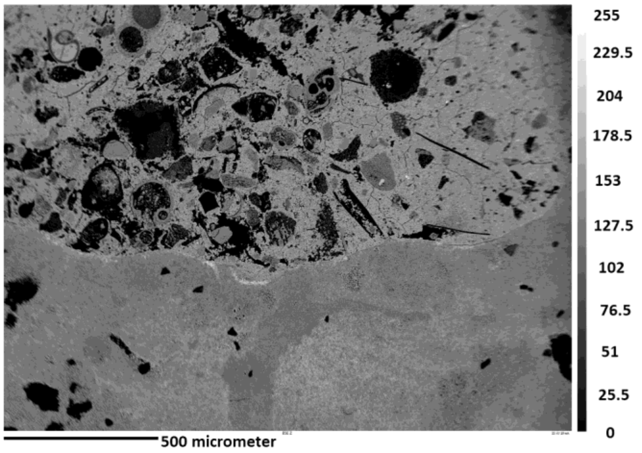

Fig. 8 — BSE image of phosphorite section with two distinct layers: A) Phosphatic and B) Carbonate. Very low count for phosphorus is observed in layer B, whereas the counts for P increases exponentially in layer A

precipitation, and (3) microbial mediation[24,25]. Primary phosphogenesis is the precipitation of carbonate fluorapatite at the sediment-water interface during diagenesis[26,27].

SEM images of the phosphorite-bearing rocks revealed clusters of microglobules resembling phosphatised bacterial structures. The phosphate is precipitated around calcite crystals in the form of micro-nodular structure, but no replacement structures were observed. The phosphate microglobules occur within the void space and appears authigenically precipitated. Such microspheres of phosphatic material have been also interpreted as fossilized bacteria in many modern and ancient phosphorites and in laboratory cultures[28-30]. Similar structures have been reported from the phosphorites of Murray ridge[19,31] which have been biologically mediated phosphogenesis. Thus the entire process involved can be interpreted as microbially-mediated precipitation of phosphorites.

Chemical analyses of the samples G-13 and G-34 show that $CaCO_3$ content (61 %) was less in the phosphatic layer compared to the compact parts (80 %) of the rock. Addition of silica and associated elements in the phosphatized area also supports the addition of silicate (clay) material to the phosphatic portion of the rock. The phosphorite precipitation is noticed within the altered parts of the limestone rock (Fig. 8). A plausible explanation for the authigenic precipitation of phosphorite within the altered parts of the limestones may be given as follows. The entire Calicut mount is covered by live corals as well as coral debris, which in turn supply abundant organic matter to the site. The microbial decomposition of organic debris during early diagenesis might have created local sub-oxic conditions and increased the pore-water phosphate, which in turn precipitated as carbonate fluorapatite within the void spaces of the

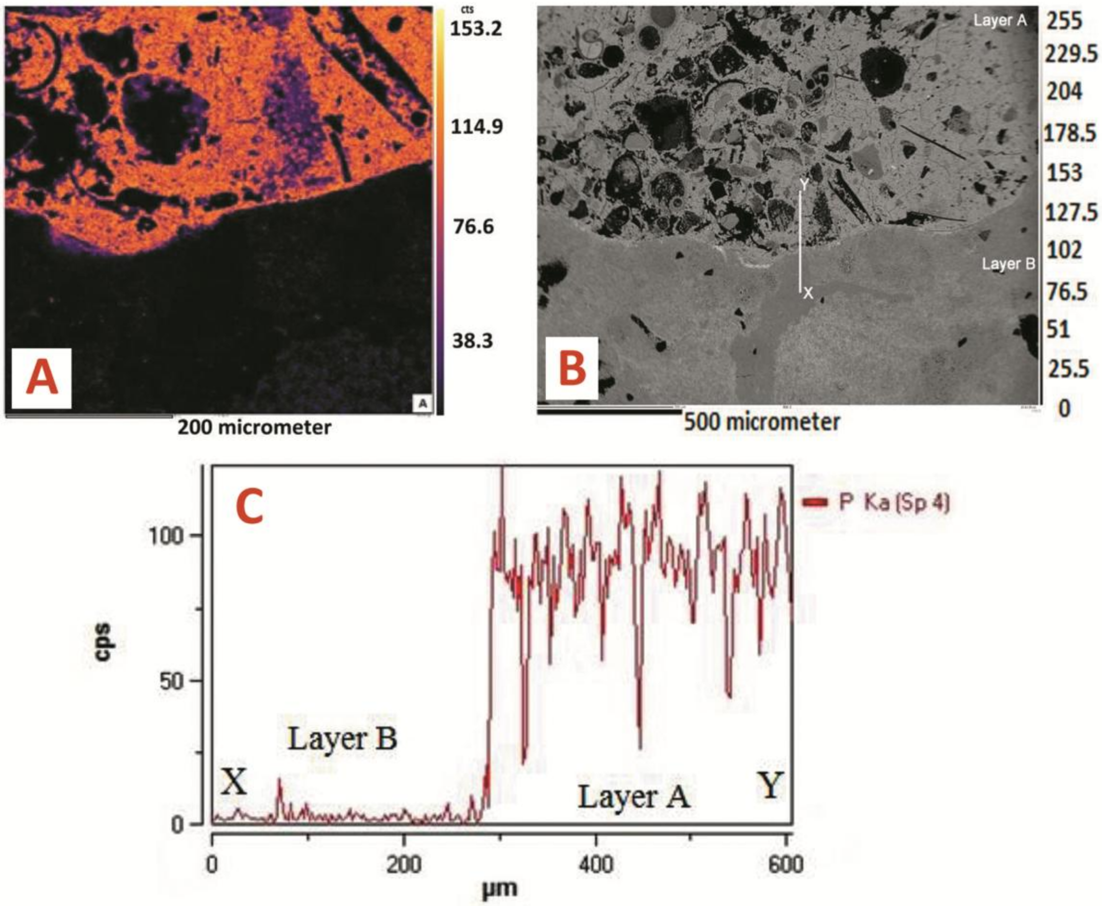

Fig. 9 — X-ray mapping of phosphorous in sample G-34: (A) X-ray compositional map for P, (B) Profile section line for P, and (C) X-rays produced profile spectrum for P

limestones[32,33]. Evaluation of the chemical, SEM and EPMA data of the phosphorite samples suggests authigenic precipitation of phosphorite under reducing conditions. The alteration of the primary rocks through solution activity under reducing conditions might have triggered the authigenic precipitation of the phosphorite.

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Conflict of Interest

The authors declare no competing or conflict of interest.

Author Contributions

GB performed investigation, formal analysis and drafted the original manuscript; AAK contributed in the conceptualization, supervision and review of the manuscript and SKS performed chemical analysis.

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