Keating, B.H., and Bolton, B.R., editors, 1992, Geology and offshore mineral resources of the central Pacific basin, Circum-Pacific Council for Energy and Mineral Resources Earth Science Series, V. 14. New York, Springer-Verlag.

PHOSPHATIC ROCKS AND MANGANESE CRUSTS FROM SEAMOUNTS IN THE EEZ OF KIRIBATI AND TUVALU, CENTRAL PACIFIC OCEAN

V. Purnachandra Rao,* W.C. Burnett

Department of Oceanography, Florida State University, Tallahassee, Florida, 32306

ABSTRACT

Phosphorite-manganese crusts were dredged from the flanks of seamounts of the Kiribati and Tuvalu EEZ (Exclusive Economic Zone) from water depths between 1450 and 2355 m. Samples from Kiribati consist of phosphatized algal laminations, coated grains, filamentous and unicellular cyanobacteria. Manganese oxide occurs in the phosphate matrix in the form of dendritic growths, as a coating on intraclasts, and as infillings in foraminifers and algal tissues. Weathered clasts derived from mafic igneous rocks are the dominant constituents in the samples from Tuvalu seamounts and phosphate occurs mainly as a cementing material for these clasts. Calcite and carbonate fluorapatite are the dominant minerals present in the matrix material of both areas.

It appears that the Kiribati seamounts were at very shallow depths during the phosphatization process, and microbial activity may have taken an active role during the diagenetic transformation of algal sediments into phosphorites. The Tuvalu samples, however, showed no evidence of shallow water conditions although some microbial influence during phosphogenesis was still apparent. Thin manganese crusts in Kiribati and thick crusts in the Tuvalu samples suggest that depth and/or length of exposure determined the relative crust thicknesses observed.

INTRODUCTION

During the Moana Wave cruise MW 86-02 in 1986, phosphorite-manganese crusts were dredged from the flanks of seamounts in the EEZ of Kiribati and Tuvalu, Central Pacific Basin, from water depths between 1450 and 2355 m. The objectives of the cruise were to investigate the origin, growth and distribution of cobalt-rich manganese and phosphate crusts and assess these materials as resources for possible future exploitation. An evaluation of the general geology of these islands was a secondary objective of the expedition. The purpose of this paper is to describe the phosphatic crusts and discuss their origin and relation to associated ferromanganese materials.

Phosphorites, phosphorite-manganese crusts, and ferromanganese crusts occur either together or separately on many seamounts in the world's oceans (Hamilton, 1956; Baturin, 1982; Hein et al., 1985). Most seamount phosphorites are thought to have formed either by replacement of carbonate or other precursor materials by phosphate during diagenesis, or by the mobilization of guano-derived phosphate initially deposited on emergent islands (Braithwaite, 1980; Cullen and Burnett, 1986; and Burnett et al., 1987). Since it was recognized that ferromanganese crusts are usually enriched in cobalt, manganese crusts on seamounts in the Central Pacific have been the object of study of several investigators (Halbach et al., 1982; Halbach and Manheim, 1984; Hein et al., 1985; Manheim, 1986; and DeCarlo et al., 1987).

Phosphorite-manganese crusts on oceanic plateau areas have also been studied by many investigators (Heezen et al., 1966; Summerhayes, 1967 and 1973; Manheim et al., 1980; and Von Rad and Kudrass, 1984) with the general conclusion that the phosphatic component is formed in variable cycles of erosion, reworking, partial dissolution and reprecipitation. The phosphatic component of the phos-

^{*}On leave from the National Institute of Oceanography, Dona Paula, Goa 403 004, India

phorite-manganese crusts found on seamounts are the least studied, but nevertheless are of considerable interest for several reasons, including: (1) the Mn component of this type of crustal material is also enriched with cobalt (Halbach and Manheim, 1984); (2) the genesis of these crusts, and the relationship between phosphate and manganese is not well understood; and (3) the alternating layers of manganese-phosphorite may reflect past changes in oceanographic conditions.

STUDY AREA AND METHODS

The Kiribati and Tuvalu Islands are in the Central Pacific Basin, lying roughly within the area between 170°E and 170°W and 5°N and 10°S (Fig. 1). The Gilbert and Ellice islands are on the western margin of the area and the Phoenix Islands are on the eastern margin. These islands are aligned in a NW-SE direction parallel to the Line Islands. Seismic reflection data of the seamounts of Kiribati have indicated that they are cone-like features similar to sub-

aerial cinder cones. The water depths at the crests of the seamounts range from 300 to 2000 m. The absolute ages of the seamounts are not available, but the sea-floor age of both island groups are believed to be Cretaceous (Keating et al., 1986; De Carlo et al., 1987).

Polished and thin sections of phosphatic rocks from seamounts in the Kiribati and Tuvalu regions (Table 1) were prepared for all samples. Thin sections were studied using a standard petrographic microscope and SEM studies were carried out with a JEOL model 840 scanning electron microscope equipped with an energy dispersive X-ray analyzer. Powdered bulk samples were analyzed for mineralogical composition from 2° to 70° 2θ at 1° 2θ/min. On a Philips X-ray diffractometer using nickel-filtered CuKα radiation. Slow scan speeds (1/2° 2θ/min) were used for XRD estimation of the structural carbonate concentration of carbonate fluorapatite (CFA) by the method of Gulbrandsen (1970).

Chemical analyses of bulk samples for P₂O₅ and F were obtained by taking 100 mg of the dried and powdered rock sample, leaching with 2N HCl, and separating the insoluble

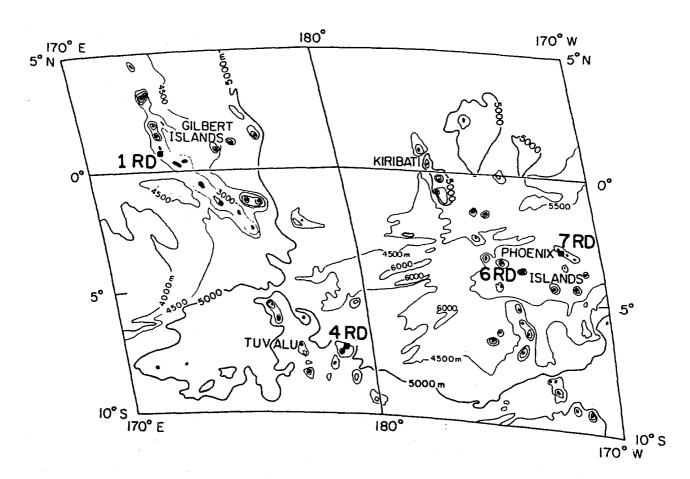


Figure 1. Map of Central Pacific Basin showing sampling locations.

residue by filtration. These leachates were diluted to the appropriate concentrations and used for both analyses. The P₂O₅ content was determined by colorimetry following the standard method of Murphy and Riley (1962). The P₂O₅ contents determined for NBS standard rocks 120b and 694 were within 2% of reported values. Fluoride was determined potentiometrically using an Orion F ion specific electrode and citrate buffer (Edmond, 1969). The accuracy of these values was within 7%.

RESULTS

Phosphatic rocks from Kiribati (stations 1 and 7)

a) Petrology

Polished sections of the rock sample from station 1 showed a phosphatized pink substrate in the basal parts

Table 1. Location and description of phosphorite-manganese crusts from Cruise MW-86-02.

Sample No	Latitude	Longitude	Water Depth (m)	Description	
			Kiribati		
1RD001-1	00° 46.58'N	173° 01.33'E	1450	Algal limestones with stains of manganese oxide on the the surface: dominantly algal fragments and calcite.	
1RD001-1		11 -	tt	Substrate for algal limestones: ironstained, phosphatized and no other skeletal components can be identified except the benthic foram <i>Lepidocyclina</i> .	
7RD011-03	02° 59.52'S	171°22.82'W	1730	Mn crust (15 mm thick) on algal limestones: phosphate replaced bioclasts.	
7RD011	n .		n	Mn crust (4 mm thick) on algal foram limestones: phosphate as well as Mn oxide replaced forams and coated grains. Botroiydal and dendritic growths of Mn oxide.	
7RD011-P	tt	Ħ	r	Mn crust (3 cm thick) on algal lime stones: fine laminations and phosphate grain between algal filaments.	
7RD011-R	tr	n	u	2-4 mm thick Mn crust on algal foram limestones: 4-6 mm thick Mn oxide layer between phosphate layers.	
7RD011-07	11	H.	11	Mn crust (6 mm thick) on algal limestones: rounded chert grains and coated grains.	
			Tuvalu		
4RD007-02	07° 24.47'S	179 °02.16'E	1620	Dominantly Mn crust (15-20 mm thick) on weathered clasts and carbonate: planktonics in the matrix.	
4RD007-21A	11	11	H	Dominantly weathered clasts and Mn crust (15-20 mm thick): planktonics in carbonate-phosphate matrix.	
4RD007-21B	n	11	Ħ	Thin (3 mm) Mn crust. Dominantly weathered clasts and phosphatized carbonate.	
6RD008-02	03° 50.23'S	173°19.74'W	2355	Thick (60 mm) Mn crust on weathered clasts and carbonate. Mn infilled forams and oxide growth around bioclasts	
6RD008-03	11	, 11	II	10-15 mm thick Mn crust: weathered rock clasts, micromanganese nodules and planktonics in the matrix.	

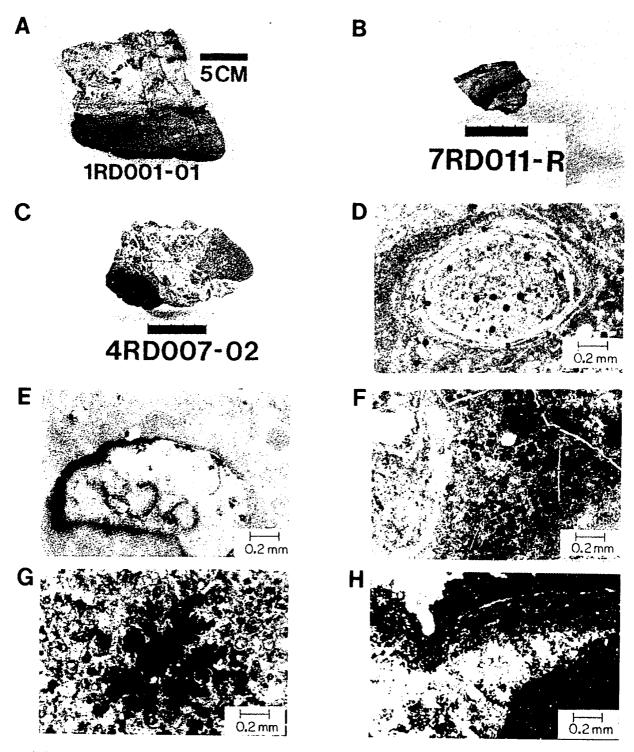


Figure 2. (A) and (B) are the polished sections of rocks sampled from Kiribati: (A) rock showing pink phosphatized carbonate as a substrate overlain by white carbonate limestone; (B) a sample characterized by alternate layers of phosphorite and manganese oxide; (C) polished section of a rock sampled from Tuvalu, showing weathered clasts embedded within a phosphate matrix; (D), (E), (F), and (G) are thin section photographs of rocks sampled from Kiribati: (D) coated grain (7RD011-07); (E) intraclasts coated by manganese oxide (7RD011-07); (F) manganese oxide distribution within the algal tissue material (7RD011); (G) dendritic growths of manganese oxide in a phosphatized carbonate matrix (7RD011-03); and (H) fine-grained phosphate separating metal oxide layers (7RD011-07).

overlain by white coralline limestone (Fig. 2A). In thin section, the pink coloring of the substrate proved to be caused by iron staining. It is difficult to identify the other skeletal components in this material except the benthic foraminifera Lepidocyclina, an index fossil of Eocene age. The white substrate of the rock consists of coralline algal fragments with occasional gastropods. Manganese oxide stains on the surface were also observed. Polished sections of the rocks from station 7 show distinct manganese oxide crusts on the outer edges and phosphatized, finely laminated structures on the interior. Discontinuous phosphate layers from 5 to 10 mm thick are present between the metal oxide layers (Fig. 2B). Thin sections show that these rocks consist of phosphatic grains and planktonic foraminifers that are bound by cryptalgal laminations. This laminated fabric interspersed with sediment particles is well-known in cyanobacterial mat activity (Monty, 1976) and is the result of concurrent finely laminated mat growth and sediment deposition. Among the phosphatic components, grains coated with micritic phosphate (Fig. 2D), similar in appearance to the coated grains reported by Peryt (1983), and phosphatic intraclasts with manganese oxide rims (Fig. 2E) are commonly observed. Coralline algal fragments, planktonic forams and fine-grained phosphate are found in the phosphatic layers present between metal oxide layers (Fig. 2H). Rounded, reddish brown chert grains are occasionally embedded in the algal layers.

Our SEM observations on freshly broken surfaces of the rocks from station 7 confirmed and expanded the previous petrologic observations. Rock cavities exhibit irregularly encrusted endolithic algal filaments (Fig. 3A) similar to those shown by Schroeder (1972). These filaments are coated by well-crystallized CFA. The filaments are empty, as shown by the cavities at the end, and the diameter of each filament is about 10 mm, with a hollow diameter of about 3 mm size (Fig. 3B). Phosphatic peloids formed by the accretion of cryptocrystalline diagenetic CFA are also present in the cavities of the rock. Tubular filaments (Fig. 3C) and straight tubes of 5 to 7 mm length enveloped by phosphatized sheaths (Fig. 3D) are also seen in the matrix. Similar structures, thought to be of cyanobacterial origin, have been reported by Krumbein (1977) in calcarcous deposits and by Soudry and Champetier (1983) in Cretaceous phosphorites from the Negev Desert, Israel. These rocks also contain phosphatized colonies of unicells of possible cyanobacterial origin. These cells range from 3 to 4 mm size, and aggregation of cells into pellets at interfaces between mats and colonies of cyanobacterial cells was observed (Fig. 4A and 4B). Phosphatic "lumps" within the phosphatized carbonate shells, marginal grain corrosion, and phosphatic borings within shells were found within the matrix (Fig. 4C). Under high magnification, these lumps appear to be an amalgamation of cyanobacterial cells (Fig. 4D). These cells are larger than those observed in other areas (Fig. 4B), confirming the observations of Zanin et al. (1985) that cavities and voids are often sites for larger organisms.

Examination of freshly fractured surfaces of these samples show that crystals morphologically resembling gypsum, with well-developed prism faces (Fig. 4E), are occasional components of these phosphorites. Gypsum crystals formed by authigenesis in the presence of organic matter are stubby and tend to lack the prismatic forms of those observed here (Sonnenfeld, 1984). Since gypsum crystals also occur on cyanobacterial filaments (Fig. 4F), they apparently have not formed after sample recovery by dehydration. Rather, the presence of these crystals indicates that shallow evaporative conditions were prevalent at some stage in the history of these phosphorites.

Manganese oxide in these samples (station 7) occurs in two modes. First, it occurs as crusts on the surface of the phosphatic rocks. The thickness of the crusts varies from surficial rinds to crusts about 15 mm thick. Secondly, manganese oxide occurs within the phosphate matrix, infilling foraminiferal chambers, replacing carbonate in algal tissue material (Fig. 2F), and accreting in the matrix in dendritic patterns (Fig. 2G). Cuspate growths of iron oxides were observed within these dendritic patterns. The manganese oxides are often distributed along fine laminations. It is clear from the internal structure (Fig. 2G) that manganese oxide is associated with the phosphatic rather than with the calcareous material, suggesting that phosphate is a preferred host for manganese. This may be due to the relative insolubility of CFA relative to calcite. Manganese oxides distributed along microlaminations in a dendritic pattern are also present (Fig. 4F). The X-ray energy dispersive analyses indicated that magnesium, manganese, calcium, and phosphorus are all abundant in these laminations, suggesting that the microlaminations are filamentous algal structures in which manganese oxide replacement has taken place.

b) Mineralogy and Geochemistry

Analysis by X-ray diffractograms of the phosphatized material shows that calcite and CFA are the major minerals present. The structural CO₂ content of CFA in all samples estimated by the peak-pair X-ray method (Gulbrandsen, 1970), is relatively high, approximately 6%. The 'a' cell dimensions are about 9.3Å indicating that the CO₃:PO₄ mole ratio of these apatites is approximately 0.22 (Table 2). The replacement of PO₄ by CO₃ changes the cell parameters of the apatite lattice in such a way that there is a decrease in the 'a' unit cell parameter with increasing carbonate substitution (McClellan and Lehr, 1969). The XRD studies of samples from the manganese oxide layer, however, showed no discernible manganese mineral peaks, probably due to the poor crystalline nature and/or the ex-

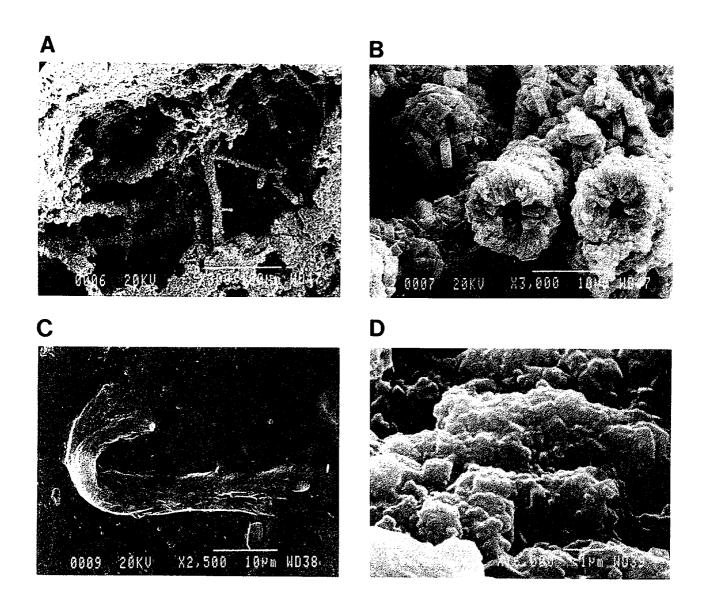


Figure 3. SEM photographs from rocks sampled from Kiribati: (A) irregularly encrusted endolithic algal filaments (7RD011-07); (B) enlarged portion of (A), showing empty filaments and well-crystallized carbonate fluorapatite adhering to filaments; (C) tubular filaments of cyanobacteria (7RD011-P); (D) straight tubes of cyanobacterial origin coated by phosphatized sheaths (7RD011-07). Energy dispersive X-ray analysis showed high calcium and phosphorus as well as minor amounts of sulfur present in these tube structures.

tremely fine grain-size of the material found in scamount manganese crusts (Burns and Burns, 1976). In addition, interference from X-ray fluorescence of the Mn-rich material may have partially obscured the diffraction peaks.

The P₂O₅ content of the Kiribati phosphorites ranged from 13 to 33% and the fluoride content varied from 2.0 to 3.8%. The F/P₂O₅ mass ratios were all in the range 0.110 to 0.129, except for one sample, which was very high at 0.15. These relatively high F contents are consistent with an-

ticipated amounts in highly substituted carbonate apatites (McClellan and Lehr, 1969).

Phosphatic rocks from Tuvalu (stations 4 and 6)

a) Petrology

These rocks consist of thick manganese oxide crusts ranging from 3 to 60 mm, and abundant weathered clasts

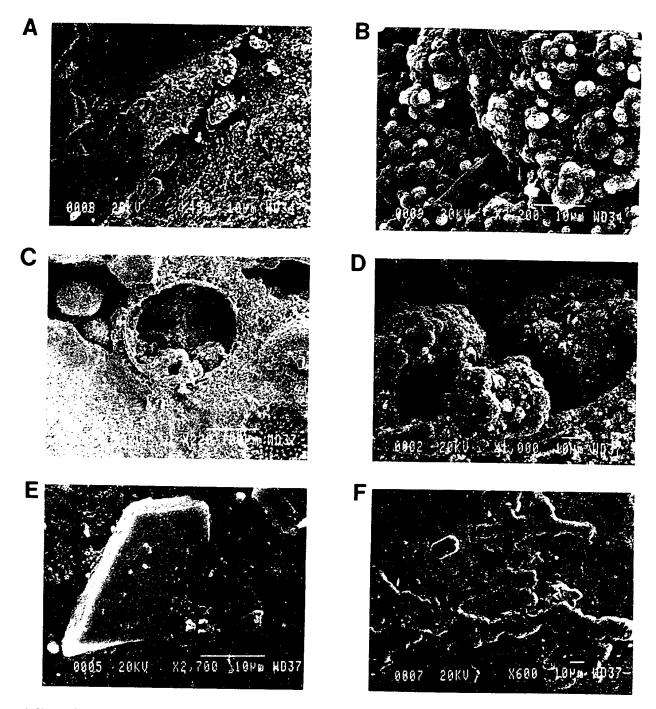


Figure 4. SEM photographs from rocks sampled from Kiribati: (A) cyanobacterial mats, coccoid unicells, and phosphate "pellets" at an interface between mat and coccoid unicells. Pelletal forms appear to be formed by the aggregation of phosphatic unicells (7RD011-P); (B) enlarged portion of (A) showing coccoid colony of cyanobacteria (X-ray analysis confirmed that the mat and unicells were phosphatic); (C) phosphate lumps within a foram shell and in cavities. Boring patterns developed within the shell chamber (lower right margin) can also be seen (7RD011); (D) enlarged portion of (C), showing that the lumps are an amalgamation of cyanobacterial unicells; (E) prismatic gypsum crystals and dendritic manganese growths (F) within a phosphate matrix (7RD011-R). X-ray analysis showed that these filaments showed high magnesium and manganese as well as calcium and phosphorus, confirming that these are algal filaments replaced by manganese and phosphate.

derived from mafic rock fragments cemented together by a carbonate-phosphate matrix (Fig. 2C). These rocks contain planktonic foraminifers as abundant components in the matrix. Clinopyroxene and plagioclase were identified in the weathered clasts. The mafic rock clasts are heavily altered and occasionally replaced by calcite, phosphate, and iron oxides.

The SEM studies revealed considerable dissolution of carbonate shell walls and borings developed within foraminiferal chambers (Fig. 5A). These borings are oriented normal to the surface (Fig. 5B). We also observed micro-dissolution features on the surfaces of the carbonate grains and subsequent formation of microgranular CFA on these surfaces (Fig. 5C). Unphosphatized coccoliths (Fig. 5D) and discosters are other components observed in the matrix.

b) Mineralogy and Geochemistry

The X-ray diffractograms show that plagioclase, apatite, hematite, goethite, and chlorite are present in these samples. The structural CO₂ content varies from 5.2 to 6.0% and the 'a' cell dimensions are about 9.3Å indicating that the CO₃:PO₄ mole ratio of the CFA is similar to the phosphorites from Kiribati (0.22). No manganese oxide mineral peaks were observed in the X-ray diffractograms of the manganese oxide crust material.

The P₂O₅ contents in these samples is similar to those of Kiribati at 18 to 30% and the fluoride content ranged from 2.3 to 3.4%. The F/P₂O₅ mass ratio varied from 0.110 to 0.124.

While the phosphorite-manganese rocks from the Kiribati seamounts displayed shallow-water fauna and thin

Table 2. Detailed mineralogy and geochemistry of the phosphatized material from the seamount samples.

Sample No.	X-ray mineralogy ¹	Structural components of CFA		P ₂ O ₅ %	F %	F/P ₂ O ₅
	·····	CO ₂ % ²	a(Å)	· · · · · · · · · · · · · · · · · · ·		
•			Kiribati	•		
IRD001-1	cal					
1RD001-1	cal and CFA	6.0	9.32	13.3	2.0	0.15
7RD011-03	CFA and cal	5.2	9.325	25.9	3.25	0.125
7RD011	CFA and cal	6.0	9.32	25.7	3.25	0.115
7RD011-P	CFA and cal	6.0	9.32	32.1	3.70	0.115
7RD011-R	CFA and cal			32.8	3.70	0.113
7RD011-R ³	CFA and cal			33.1	3.79	0.11
7RD011-07	CFA			29.3	3.74	0.127
7RD011-07 ⁴	opal-CT and sid					
			Tuvalu			
4RD007-02	CFA and cal			18.6	2.4	0.129
4RD007-21A	plag, CFA, cal goet and chlo					
4RD007-21B	CFA and cal	6.0	9.32	30.4	3.4	0.112
6RD008-02	CFA and cal	5.2	9.325	24.1	2.9	0.12
6RD008-03	CFA cal and plag			18.5	2.3	0.124

¹minerals listed in approximate order of abundance: cal – calcite, CFA – carbonate fluorapatite; plag – plagioclase; goet – goethite; chlo – chlorite, and sid – siderite

and sid. – siderite.

²Gulbrandsen (1970) X-ray peak-pair method.

³phosphate layer in between metal oxide layers.

rounded chert grain found embedded within algal layers.

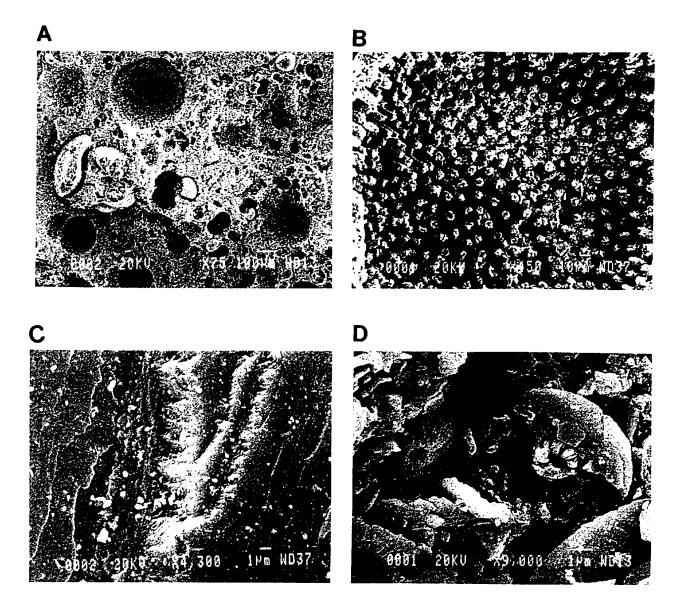


Figure 5. SEM photographs from rock sample 4RD007-02, from a seamount in Tuvalu: (A) photograph illustrating dissolution of carbonate shell walls; (B) enlarged portion of (A) showing phosphatized casts developed within foraminiferal chambers (X-ray analysis confirmed that these casts are rich in calcium and phosphorus); (C) microdissolution features on a carbonate grain surface together with small grains formed on these surfaces; and (D) unphosphatized coccoliths within the matrix material.

manganese oxide crusts, the samples from the Tuvalu seamounts showed open-ocean fauna and thick manganese crusts. However, samples from both areas displayed dissolution of grain surfaces and boring patterns developed within shell chambers. The principal geochemical and mineralogical features of samples from both areas did not show significant variation although the abundance of CFA is somewhat lower in the Tuvalu seamounts.

DISCUSSION

Thin section observations and SEM studies have revealed that endolithic algae and filamentous and unicellular cyanobacteria are widely distributed in the Kiribati phosphorites. Prismatic gypsum, larger foraminifera (Ex. Lepidocyclina), and gastropods are also associated with

these samples. This indicates that these sediments must have accumulated when the seamount was at intertidal or subtidal depths. Cell-like structures of possible cyanobacterial origin inside the carbonate shells, marginal grain corrosion on the calcareous grains and the different boring patterns in these phosphorites (Figs. 4C,4D) appear to be caused by the action of algae. Klement and Toomey (1967) and Golubic (1973) state that certain boring and perforating algae are highly destructive of carbonate shells and coastal limestones, and their optimal distribution would be in shallow stagnant environments at depths up to about 20 m. Phosphate grains bound by cryptalgal laminations, phosphate intraclasts and grains coated by layers of micritic phosphate also suggest that the phosphatization occurred during shallow water diagenesis. X-ray energy-dispersive analysis has confirmed that the cyanobacterial cells and filaments present in these rocks are completely phosphatized.

Cyanobacteria are known to fix high concentrations of phosphorus during their metabolic activity (Azad and Borchardt, 1970). It is also known from the experimental studies of Kobluk and Risk (1977) and from studies of calcareous deposits (Krumbein, 1968; Klappa, 1979) that algae are not directly involved in calcification, and that precipitation of carbonate takes place mostly on dead filaments. We suggest that, during shallow-water diagenesis of these carbonate sediments, the decay of cyanobacterial cells and filaments of algae induced phosphate precipitation. Hence, the concentration and subsequent release of phosphate within the sediment constituted the microbial role in the formation of these phosphorites. Cyanobacterial influence in phosphogenesis has been suggested by Soudry and Champetier (1983) and Southgate (1986). The well-crystallized phosphate crystals, found on endolithic algal filaments with empty cavities (Fig. 3B), and the phosphatized sheath on cyanobacterial filaments (Fig. 3D) might suggest that phosphatization took place in the early stages of the decay of these filaments. These observations also imply that the phosphate mineralization of these filaments is a direct process rather than replacement of carbonate which preexisted on filaments. These organic filaments may not only be the source for phosphate, but may also serve as favorable sites for phosphate mineralization, as suggested by Southgate (1986).

Our studies have revealed that appreciable concentrations of phosphorus occur in the fossilized cells of possible cyanobacterial origin. High concentrations of phosphate in bacterial structures (cocco-like and bacilli forms) have been reported earlier by Cayeux (1936), Oppenheimer (1958), O'Brien et al. (1981), Riggs (1982), Prevot and Lucas (1986) and Zanin et al. (1985). To our knowledge, our observations of these structures are the first reported for seamount or "open-ocean" phosphorites. We suggest that the shallow-

water phosphorites (Kiribati samples) were formed during early diagenesis of algal laminated sediments. Cyanobacteria were involved in the evolution of these phosphorites either as a source for phosphate or a suitable surface for precipitation, or both. Phosphate released to interstitial waters subsequently replaced carbonate shell materials, precipitated into cryptocrystalline aggregates in the form of pellets in rock cavities, and produced the coatings around phosphate pellets.

The structural CO₂ content of the CFA is about 6%, slightly higher than the CO₂ content of most marine phosphorites (Kolodny, 1981). This may be related to the presumed high carbonate content of the predecessor materials (Birch, 1980). The CO₃:PO₄ mole ratio of about 0.22 is close to values reported for Chatham Rise phosphorites (~0.25) where the phosphatization occurred within a carbonate-rich matrix (Von Rad and Kudrass, 1984).

Phosphorite-manganese crusts of the Tuvalu seamounts were dredged from greater depths than the Kiribati samples, and phosphate in these crusts occurs mainly as a cementing material for hyaloclastites, derived from the weathering of volcanic materials. The cementing material consists of open-ocean fauna such as planktonic foraminifera and coccoliths. Characteristic features such as the dissolution of calcareous grain surfaces, microbial borings within the carbonate grains, and micro-dissolution structures on calcareous grain surfaces (Fig. 5A, B, C and D) indicate that the destruction of carbonates has taken place by microorganisms during diagenesis. Similar observations were reported by Lamboy (1987) for North African phosphorites, which he interpreted as indicative of a microbial role in phosphogenesis. Thus, microbial activity may also have been partially responsible for the phosphatization of these deep water samples.

Ferromanganese oxide occurs both as a matrix material and as crusts on these phosphorites. Two mechanisms can be proposed for the distribution of manganese oxide within the phosphatized matrix. Empty filaments and microbial borings resulting from algal action are commonly observed in phosphorites. Manganese oxide might have replaced these borings and infilled the filaments as a secondary precipitate. Alternatively, manganese and iron released to the interstitial waters prior to sulfate reduction during early diagenesis might have precipitated in algal channels present within the sediment. If the latter was the case, manganese oxide and phosphate formation may have been contemporaneous within the matrix material. Alternatively, if the manganese oxide is a secondary replacement, the cuspate iron oxide structures within the dendritic growths of manganese oxide, and the occurrence of manganese oxide as a coating on intraclasts, cannot be explained. We conclude, therefore, that manganese was distributed during early diagenesis with some secondary replacement occurring along algal laminations. Pratt and McFarlin (1966) and Manheim et al. (1980) suggested that both replacement type and diagenetic manganese oxide were present in manganese-phosphorite crusts of the Blake Plateau. The crust-like manganese oxides that occur on these phosphorites seem similar to those reported from other open-ocean environments and are most likely of hydrogenetic origin.

SUMMARY AND CONCLUSIONS

Our studies of the phosphorite-manganese crusts from Kiribati seamounts suggest that (a) the paleodepths of the seamounts were very shallow, probably intertidal or subtidal, during phosphatization; (b) endolithic algae and cyanobacteria were influential in the early diagenesis of carbonate sediments, which took place when the seamount was at shallow depths; (c) organic filaments may have acted as both a source and a substrate for phosphate mineralization; and (d) early diagenetic as well as replacement-type manganese oxides appear to be present in the phosphatic matrix.

Study of the phosphorite-manganese crusts from Tuvalu seamounts shows that (a) weathered clasts from mafic rocks are the main constituents of these samples, whereas the phosphorite occurs as a cementing material for the clasts; (b) phosphatized pelagic fauna are the main constituents of the cementing material; (c) boring patterns and destruction of carbonate grains are similar to those in the Kiribati samples, possibly indicating microbial participation during phosphogenesis; and (d) manganese crusts are thicker than in the Kiribati samples, indicating that growth rates are faster at deeper depths, or these samples are significantly older compared to those from Kiribati.

ACKNOWLEDGMENTS

The authors are grateful to Barbara Keating and Eric De Carlo of the University of Hawaii for providing the samples upon which this study is based. Peter Southgate, Frank Manheim, and two anonymous reviewers provided many valuable suggestions on the earlier draft of this manuscript. William Landing, Koh Harada, Philip Chin, and Tom Seal of FSU (Florida State University) provided valuable laboratory assistance. We also thank Ms. Sandy Silver and Ms. Kim Riddle of the electron microscope facility at FSU for their help in the SEM studies. Financial support for W.C.B. was provided by a grant from the National Science Foundation (OCE 8520724). Mr. V.P. Rao wishes to thank the Director, National Institute of Oceanography (NIO), India for providing leave and to UNESCO for

providing a travel grant to visit FSU where this study was completed. He is also thankful to Mr. P. S.N. Murty and Mr. R.R. Nair of NIO for their encouragement.

REFERENCES

- Azad, H.C., and J.A. Borchardt, 1970, Variations in phosphorus uptake by algae: Environmental Science and Technology, v. 4, p. 737-743.
- Baturin, G.N., 1982, Phosphorites on the Sca Floor. New York, Elsevier Science Publishing Company, 343 p.
- Birch, G.F., 1980, A model of penecontemporaneous phosphatization by diagenetic and authigenic mechanisms for the western margin of southern Africa, in Marine Phosphorites, Y.K. Bentor ed.: Tulsa, OK, Society of Economic Paleontologists and Mineralogists, Special Publication, 29, p. 79-100.
- Braithwaite, C.J.R., 1980, The petrology of the oolitic phosphorites from Esprit (Aldabra), western Indian Ocean, Philosophical Transactions of the Royal Society of London, B, v. 288, p. 511-540.
- Burns, R.G., and V.M. Burns, 1976, Mineralogy, in G.P. Glasby, ed., Marine Manganese Deposits: Amsterdam, Elsevier, p. 185-248.
- Burnett, W.C., D.J. Cullen, and G.M. McMurtry, 1987, Open-ocean phosphorites: In a class by themselves?, in P.G. Teleki, M.R. Dobson, J.R. Moore and U. Von Stackelberg, eds., Marine Minerals: Advances in Research and Resource Assessment: Tokyo, D. Reidel Publishing Company, p. 119-134.
- Cayeux, L., 1936, Existence de nombreuses bacteries dans les phosphates sedimentaires de tout age: C. R. Acad. Sci. Paris. v. 23, p. 1198–1200.
- Cullen, D.J., and W.C. Burnett, 1986, Phosphorite associations on seamounts in the tropical southwest Pacific Ocean: Marine Geology, v. 71, p. 215-236.
- DeCarlo, E.H., G.M. McMurtry, and K.H. Kim, 1987, Geochemistry of ferromanganese crusts from the Hawaiian Archipelago I. Northern survey areas. Deep-Sca Research, 34, p. 441-467.
- Edmond, C.R. 1969, Direct determination of fluoride in phosphate rock samples using the specific ion electrode: Bulletin Analytical Chemistry, v. 41, p. 1327-1328.
- Golubic, S., 1973, The relationship between blue-green algae and carbonate deposits, in N.G. Carr and B.A. Whitton, eds., The Biology of the Blue-Green Algae: University of California Press. p 434-473.
- Gulbrandsen, R.A., 1970, Relation of carbon dioxide content of apatite of the Phosphoria Formation to regional facies: Washington, DC, U.S. Geological Survey. Professional Paper 700-B, p. B9-B13.
- Halbach, P., F.T. Manheim, and P. Otten, 1982, Co-rich ferromanganese deposits in the marginal seamount regions of the Central Pacific Basin - results of the MidPac '81: Erzmetall, v. 35, p. 447-453.
- Halbach, P., and F.T. Manheim, 1984, Potential of cobalt and other metals in ferromanganese crusts on seamounts of the Central Pacific Basin: Marine Mining, v. 4, p. 319-336.
- Hamilton, E.L., 1956, Sunken Islands of the Mid-Pacific Mountains: Boulder, CO, Geological Society of America, Memoir 64, 97 p.
- Heczen, B.C., B. Glass, and H.W. Menard, 1966, The Manihiki Plateau, Deep-Sea Research, v. 13, p. 445-458.
- Hein, J.R., F.T. Manheim, A.S. Schwab, C.L. Daniel, R.M. Bouse, L.M. Morgenson, R.E. Sliney, D. Clague, G.B. Tate and D.A. Cacchione, 1985, Geological and geochemical data for seamounts and associated ferromanganese crusts in and near the Hawaiian, Johnston Island, and Palmyra Island Exclusive Economic Zones: Menlo Park, CA, U.S. Geological Survey File Report, 85-292, 129 p.
- Keating, B., B. Bolton and Shipboard Party, 1986. Initial report of 1986 R/V MOANA WAVE cruise MW-86-02 in the Kiribati/Tuvalu region, Central Pacific Ocean, CCOP/SOPAC Cruise Report. 121, SOUTHPAC 1986.
- Klappa, C.F., 1979, Calcified filaments in Quaternary calcretes: Organomineral interactions in the subaerial vadose environment: Journal of Sedimentary Petrology, v. 49, p. 955-965.

- Klement, K.W., and D.F. Toomey, 1967, Role of the blue-green alga Girvanella in skeletal grain destruction and lime-mud formation in the Lower Ordovician of west Texas: Journal of Sedimentary Petrology, v. 37, p. 1045-1051.
- Kobluk, D.R., and M.J. Risk, 1977, Calcification of exposed filaments of endolithic algae, micrite envelope formation and sediment production: Journal of Sedimentary Petrology, v. 47, p. 517-528.
- Kolodny, Y., 1981, Phosphorites, in C. Emiliani, ed., The Sea, Vol. 7: New York, Wiley & Sons, New York, p. 981-1023.
- Krumbein, W.E., 1968, Geomicrobiology and geochemistry of the Nari-Lime Crust (Israel), in G. Muller and G.M. Friedman, eds., Developments in Carbonate Sedimentology in Central Europe: Berlin, Springer-Verlag. p. 138-147.
- Krumbein, W.E., 1977, Primary production, mat formation and lithification: contribution of oxygenic and facultative anoxygenic cyanobacteria, in E. Flugel, ed., Fossil Algae: Recent results and developments: Berlin, Springer-Verlag, p. 37-56.
- Lamboy, M., 1987, Genesis of granular phosphorites, clues gathered from study of grains including foraminifers: importance and modes of precipitation: C.R. Acad. Sc. Paris, v. 304, p. 435-440.
- Manheim, F.T., 1986, Marine cobalt resources: Science, v. 232, p. 600-608.
- Manheim, F.T., R.M. Pratt, and P.F. McFarlin, 1980, Composition and origin of phosphorite deposits of the Blake Plateau, in Y.K Bentor, ed., Marine Phosphorites: Tulsa, OK, Society of Economic Paleontologists and Mineralogists, Special Publication, 29, p. 117-129.
- Manheim, F.T., P. Popenoe, W. Siapno, and C. Lane, 1982, Manganese-phosphorite deposits of the Blake Plateau, in P. Halbach and P. Winter, eds., Marine Mineral Deposits New Research Results and Economic Prospects: Proceedings of the Clausthaler Workshop, Republic of Germany: Verlag Gluckauf, p. 9-44.
- McClellan, G.H., and J.R. Lehr, 1969, Crystal chemical investigation of natural apatites: American Mineralogist, v. 54, p. 1374-1391.
- Monty, C.L.V., 1976, The origin and development of cryptalgal fabrics, in M. R. Walter, ed., Stromatolites, Developments in Sedimentology: Elsevier Science Publishing Company, p. 193-249.
- Murphy, J., and J.P Riley, 1962, A modified single solution method for determination of soluble phosphate in natural waters: Analytica Chimica Acta, v. 27, p. 31-36.
- O'Brien, G.W., J.R. Harris, A.R. Milnes, and H.H. Veeh, 1981, Bacterial origin of East Australian continental margin phosphorites: Nature, v. 294, p. 442-444.

- Oppenheimer, C.H., 1958, Evidence of fossil bacteria in phosphate rocks, Institute of Marine Science Publication, v. 5, p. 156-159.
- Peryt, T.M., 1983, Coated Grains: Berlin, Springer-Verlag, 660 p.
- Pratt, R.M., and P.F. McFarlin, 1966, Manganese pavements on the Blake Plateau: Science, v. 151, p. 1080-1082.
- Prevot, L., and J. Lucas, 1986, Microstructure of apatite-replacing carbonate in synthesized and natural samples: Journal of Sedimentary Petrology, v. 56, p. 153-160.
- Riggs, S.R., 1982, Phosphatic bacteria in the Neogene phosphorites of the Atlantic coastal plain continental shelf system: IGCP Project 156 Phosphorite Newsletter, n. 11, p. 34.
- Schroeder, J.H., 1972, Calcified filaments of an endolithic alga in Recent Bermuda reefs: Neues Jahrb. Geol. Palaeont. Monatsch, v. 1, p. 16.33
- Sonnenfeld, P., 1984, Brines and Evaporites: London, Academic press, 615 p.
- Soudry, D., and Y. Champetier, 1983, Microbial processes in the Negev phosphorites (Southern Israel): Sedimentology, v. 30, p. 411-423.
- Southgate, P.N., 1986, Cambrian phoscrete profiles, coated grains, and microbial processes in phosphogenesis: Georgina basin, Australia: Journal of Sedimentary Petrology, v. 56, p. 429-441.
- Summerhayes, C.P., 1967, Manganese nodules from the Southwest Pacific, New Zealand: Journal of Geology and Geophysics, v. 10, p. 1372-1381.
- Summerhayes, C.P., 1973, Distribution, origin and economic potential of phosphate sediments from the Agulhas Bank, South Africa: Translations Geological Society of South Africa, v. 76, p. 271.
- Von Rad, U., and H.R. Kudrass 1984, Phosphorite Deposits on the Chatham Rise, New Zealand, R.V.Sonne Cruise SO-17, 1981: Geologisches Jahrbuch Reihe D, Heft 65.
- Zanin, Y.N., S.V. Letov, N.A.Krasil'nikova, and Y.V Mirtov, 1985. Phosphatized bacteria from Crctaceous phosphorites of East-European platform and Paleocene phosphorites of Morocco, in J.Lucas and L. Prevot, eds, Sciences Geologiques Memoire "phosphorites" VI International field workshop and seminar on phosphorites IGCP 156, v. 77, p. 79-81.