Graduate Student Theses, Dissertations, & Professional Papers

Graduate School

1967

# Phosphatic and oolitic sediments of the Georgia continental shelf

David R. Pevear
*The University of Montana*

PHOSPHATIC AND OOLITIC SEDIMENTS

OF THE

GEORGIA CONTINENTAL SHELF

by

David R. Pevear

B.A. Allegheny College, 1962
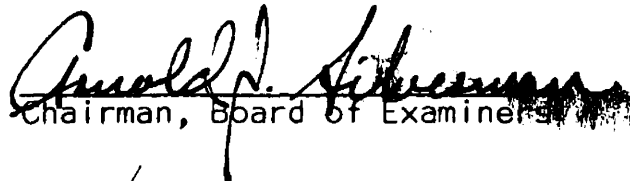
Presented in partial fulfillment of
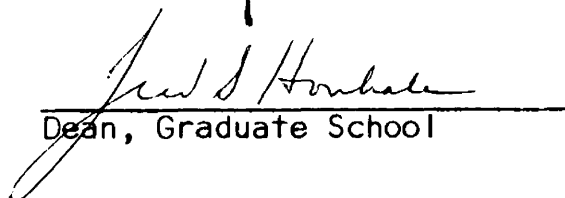the requirements for the degree of

Master of Science

University of Montana

1967

Approved by:

Chairman, Board of Examiners

Dean, Graduate School

APR 2  1967
Date

UMI Number: EP38303

UMI

Dissertation Publishing

UMI EP38303

ProQuest

# OOLITES ON THE GEORGIA CONTINENTAL SHELF EDGE

BY

ORRIN H. PILKEY, DETMAR SCHNITKER AND D. R. PEVEAR

# OOLITES ON THE GEORGIA CONTINENTAL SHELF EDGE[1,2]

ORRIN H. PILKEY
Duke University, Durham, North Carolina,

DETMAR SCHNITKER
University of North Carolina, Chapel Hill, North Carolina,

AND D. R. PEVEAR
Montana State University, Missoula, Montana

## ABSTRACT

Aragonitic oolites (ooids) are present as a minor constituent of Georgia outer continental shelf and upper slope sediments. They are found at depths between about 35 and 150 meters and are most abundant in a north-south band at the continental shelf break. Oolites make up at a maximum, about 14% of the total sediment. Associated shallow water foraminifera and a carbon 14 date of 26,000 years B. P. indicate the origin of these oolites at a time of lowered Pleistocene sea level.

## INTRODUCTION

Calcareous oolites (ooids) are a fairly abundant constituent of ancient limestones and are important because they reflect a specific environment. This environment is one of warm, shallow, agitated waters, supersaturated in calcium carbonate (Newell, Purdy and Imbrie, 1960).

The occurrence of oolites in Recent carbonate bank sediments is well documented with many examples but their presence in so called "non-carbonate" sediments is much less common. Stetson (1938), as a result of a reconnaissance study, made the interesting observation that oolites occur in some Atlantic shelf sediments of the Southern United States. A similar occurrence of oolites was noted by Subba Rao (1964) in outer shelf sediments off the East Coast of India. Both Stetson and Subba Rao conclude that the oolites were formed during lowered sea levels of the Pleistocene. The purpose of this study is to investigate in detail the nature and areal distribution of oolites on the continental shelf of Georgia.

## METHODS

Four detailed linear sampling traverses were made across the continental shelf and shelf break of Georgia. Selected samples from the central and inner shelf and all samples available from the outer shelf and upper slope were examined microscopically. Thin sections were made of oolites from selected samples. Oolite grain size determinations were accomplished by counting oolites in separate size fractions. Mineralogical deter-
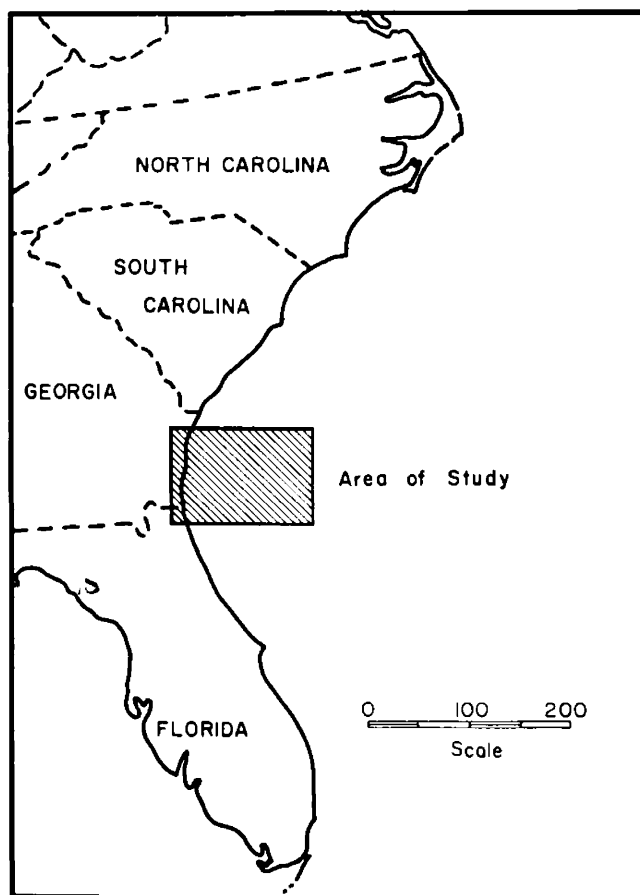


Fig. 1.—Index map of the study area.

minations were made using standard X-ray diffraction techniques. A radiocarbon date was obtained from Isotopes Incorporated.

## REGIONAL SETTING

Figure 1 is an index map showing the study area. Figure 2 is a map showing oolite distribu-
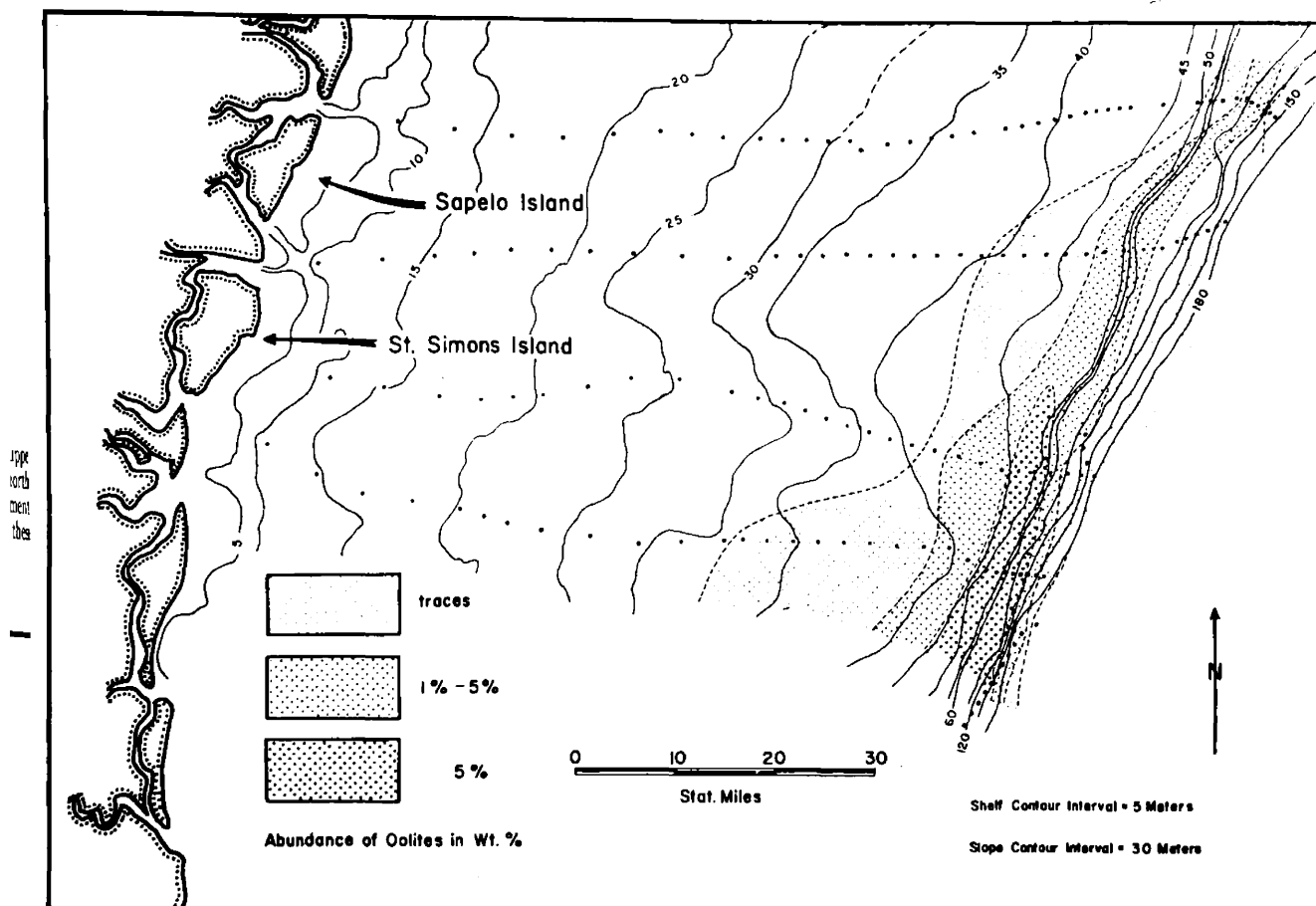
FIG. 2.—Map of the study area showing the distribution of oolites in Georgia shelf sediments. Bottom topography taken from Pilkey and Giles (1965).

tion and bottom topography. The surface of the continental shelf of Georgia slopes gently seaward to depths ranging from 50 meters in the southern portion of the study area to 75 meters in the north. Shelf width ranges from 130 to 145 kilometers. According to Gorsline (1963) most of the shelf is covered by relict (Pleistocene) sands of fine to medium grain size containing a significant carbonate fraction which usually falls between 10 and 40 percent of the total sample. Upper slope sediments consist of silt and clay size detrital material with a large pelagic Foraminifera fraction (Wilcoxin, 1964). Slope material usually contains greater than 50 percent calcium carbonate.

### RESULTS

The band of maximum oolite concentration occurs approximately at the shelf edge (fig. 2).

On the northern traverse, however, the oolite band is found below the shelf break, and the depth of greatest oolite abundance is between 75 and 115 meters.
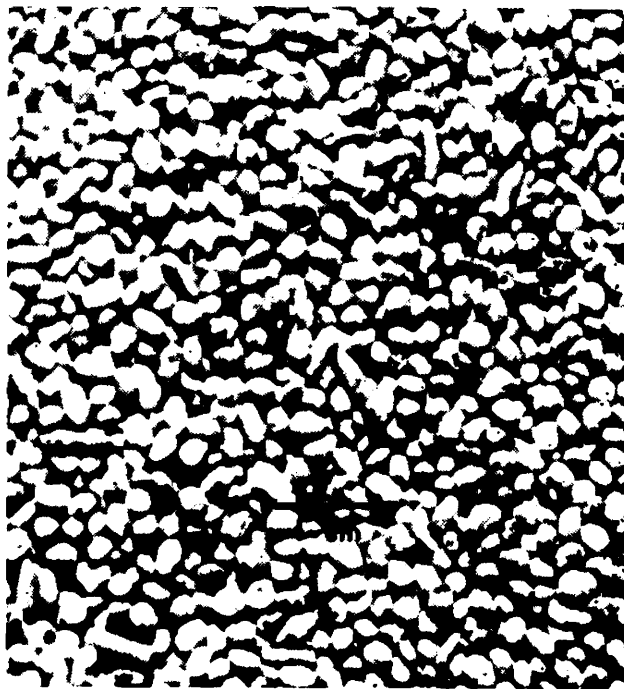
FIG. 3.—Oolites and some fecal pellets and shell fragments concentrated from a single sample.
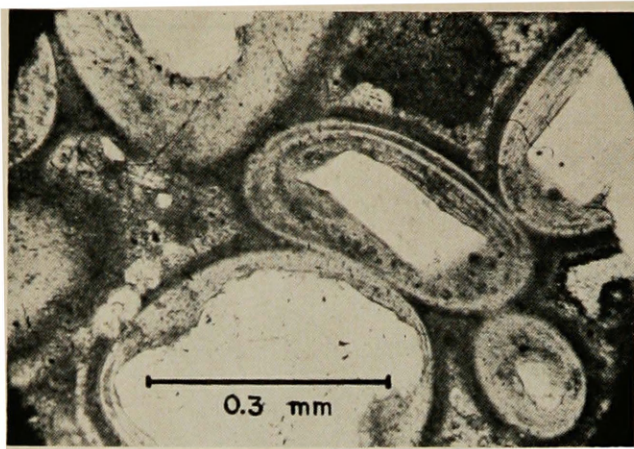
**(a)**
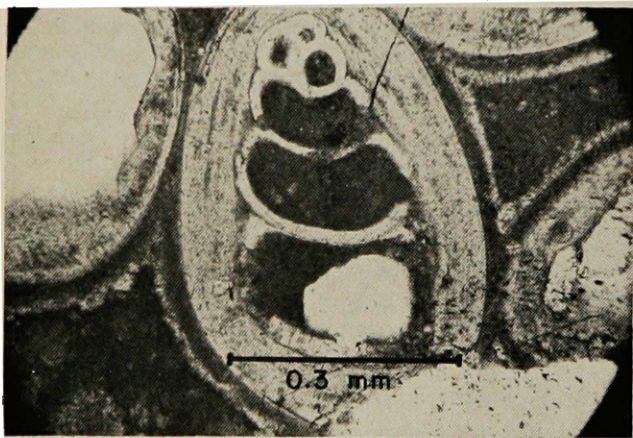


**(b)**
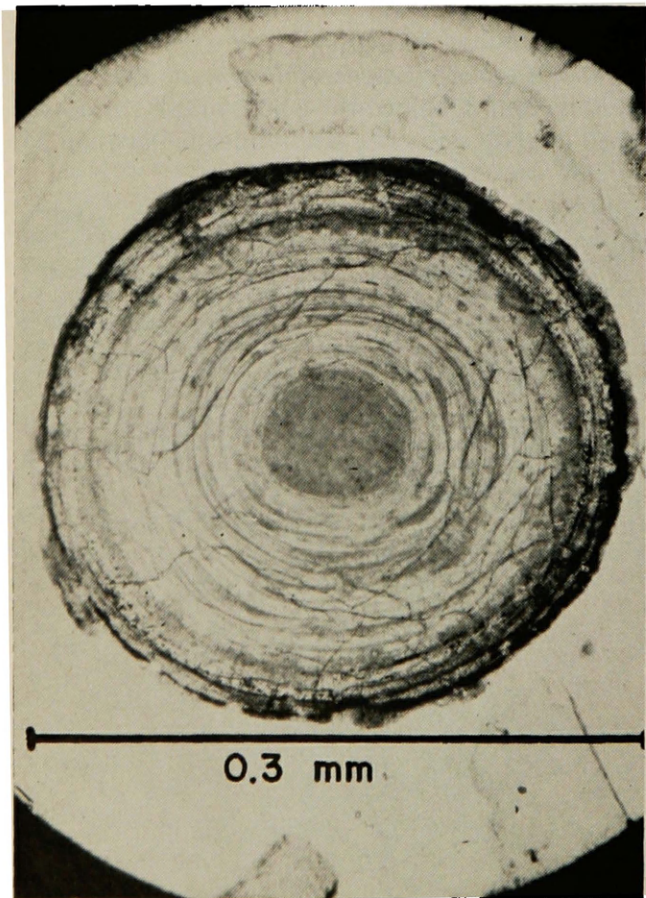


**(c)**

Oolite concentration decreases landward and seaward. The shallowest occurrence of significant numbers of oolite grains (greater than 0.1 percent of the total sediment) is at depths of around 35 meters. At the shelf edge oolites reach an observed maximum of close to 14 percent of the total sediment. The deepest occurrence noted is about 150 meters. As can be seen in figure 1, the abundance of oolites is greatest in the south.

Figure 3 is a photograph showing oolites concentrated from a shelf edge sample. Typically the grains are spherical to slightly ovoid in shape and have either a dull surface or a high surface gloss which may be an abrasional phenomenon according to Newell, Purdy, and Imbrie (1960). A few grains are white to amber colored but most exhibit various shades of blue-gray, blue-black to gray-brown. Stetson (1938) noted that some of the oolites contain about 1 percent $P_2O_5$ which may account for the blue-black color.

Thin sections of oolites clearly show the characteristic concentric lamination and the pseudo-uniaxial interference cross. The grains are composed of aragonite. Quartz grains of various sizes are the nuclei for most of the oolites (fig. 4A), but other nuclei are shell fragments, foraminifera tests, small benthic gastropods (fig. 4B) and fecal pellets (fig. 4C). Tubes of boring algae penetrate some oolites. Corners of the quartz grains frequently protrude through the calcareous cover, indicating either abrasion or incomplete precipitation.

The median grain size of oolites is typically similar to that of the enclosing sediment. In 11 selected samples the average median grain size of oolites is 0.38 mm (medium sand) with a range from 0.20 mm to 0.50 mm.

Calcareous fecal pellets are commonly associated with the oolites. Often these pellets are elongate and can be distinguished from the oolites on this basis. However, this distinction cannot be used on more equidimensional pellets which must be examined by thin section observation or by the presence of a clayey acid insoluble residue, characteristic of fecal pellets and usually not present in oolites. Some fecal pellets can be seen in figure 3.

It was noted that samples containing an

FIG. 4.—Thin sections of oolites. A and B are photos of thin sections of the oolitic sandstone discussed in text. Oolites are medium sand size. A. Quartz grain nuclei, B. gastropod nucleus, C. fecal pellet nucleus. These oolites are between 0.3 and 0.4 mm in diameter.
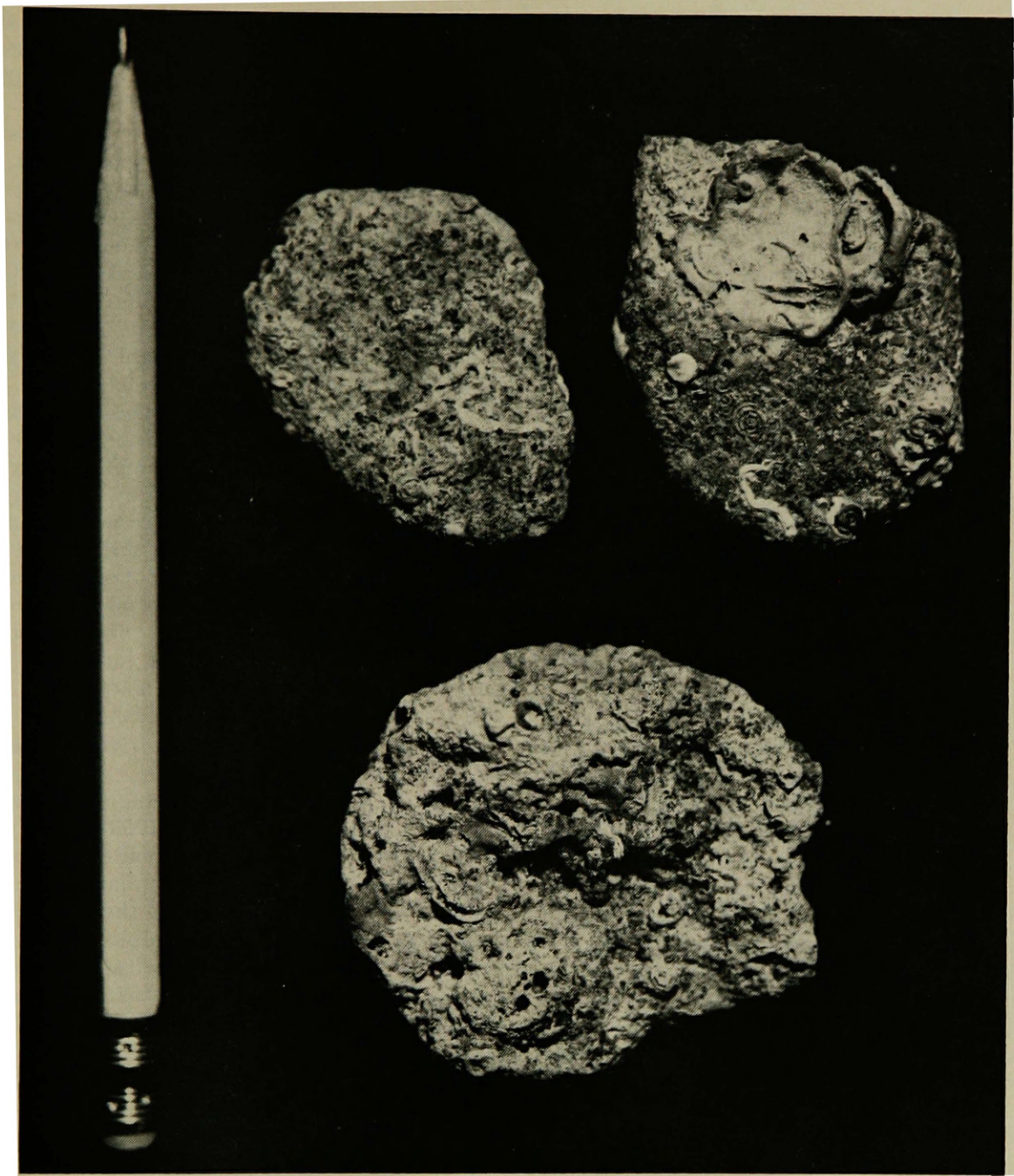
FIG. 5.—Rounded oolitic sandstone pebbles from the Georgia shelf edge.

...ndance of oolites, also contained shallow ...ter foraminifera. These are *Miliammina* sp., *M. fusca* (Brady), *Nodobaculariell atlantica* ...shman and Bermudez, *Sigmoilina centil-* *...um* (d'Orbigny), many species of *Quinquelo-* *...ina* and some Peneroplidae. The foraminifera ...readily be separated from the indigenous ...ns on the basis of their preservation. Most of ...m are stained, ranging from an opaque amber ...wn to gray and blue black in color. Com-...ly these tests are fragmental and polished.

...second mode of occurrence of oolites on the ...rgia shelf edge was noted in the form of ...ral flat well rounded pebbles obtained in a biological trawl. The pebbles consist of calcareous cemented quartz and oolite grains. The oolites in the sandstone pebbles have identical characteristics with those previously described. The pebbles are well cemented and when fractured often break across oolite but not quartz grains. The cement is micritic in texture. A mineralogical analysis of one of the pebbles indicated that the calcareous portion consists of 55 percent aragonite, 27 percent high magnesium calcite and 18 percent low Mg calcite. Three of these pebbles (with encrusting organisms) are shown in figure 5, and figures 4A and 4B show thin sections having both oolites and cement.

## DISCUSSION

Oolites form today in depths of less than 10 feet. According to Newell, Purdy, and Imbrie (1960) the optimum depth of formation may be less than 6 feet. Thus the presence of oolites in outer shelf sediments is an indication of former shoreline conditions. On the Bahama Banks oolites are forming primarily along the shallow margins, and in part the edge of the Georgia Continental Shelf may be an analogous situation. Certainly wave energy might be expected to be relatively high here due to impinging deep water waves, undiminished by friction on a wide shallow, re-entrant shelf. This would furnish the requisite turbulence for oolite formation. On the Bahama Banks, flood tide flow of $CO_2$ rich water onto the banks over marginal shoals probably furnishes the $CaCO_3$ (Newell, Purdy, and Imbrie, 1960). Topographic evidence of a pre-existing marginal shoal and landward lagoon is missing on the Georgia shelf, but this evidence could have been destroyed during the last sea level rise.

Conditions favorable for oolite formation may have been aided by the possible close proximity of warm Gulf Stream waters when sea level coincided with the shelf edge. However, preliminary work on sediments from the North Carolina shelf, particularly Onslow Bay, indicates the presence of oolites in inner shelf sediments. Similarly, Stetson (1938) noted that oolites are widely distributed in Florida Atlantic shelf sediments. It is unlikely that the Gulf Stream directly influenced such shallow areas.

Because the band of maximum oolite concentration is found at different depths on the Georgia shelf edge, it is apparent that all the oolites were not formed simultaneously. In order to ascertain an age of the oolite forming conditions, a radio-carbon date was obtained on a sample of oolites separated from sediment taken at depths of 79 and 104 meters from the central portion of the study area. A composite sample was necessary to obtain sufficient numbers of oolites for analysis. A source of possible error of the radiocarbon date is the oolite enclosed calcareous material which could be significantly older than its surrounding material. However, most nuclei are quartz grains which would not affect the date.

The date obtained for this composite sample is 26,000 (+4,000, −2500 years B. P. Conclusions based on single radiocarbon dates are tenuous at best, and in this case the reliability of the date is further weakened by the composite nature of the sample and the aforementioned possible nucleus contaminants. The reliability of the date, however, is sufficient to state that the oolites are not forming at the present time. Dating material from single sample locations and using only the outer oolitic layers of the grains should result in much more meaningful ages.

The origin of the rounded oolitic sandstone pebbles is a most interesting problem (fig. 4A, 4B and 5). One strong possibility is that this sandstone is a former beach rock formed at the same time as the oolite band under intertidal conditions similar to those described by Ginsburg (1953). One important difference between the Dry Tortugas beach rock described by Ginsburg (1953) and the Georgia shelf pebbles is the mineralogy of the calcareous cement. The cement of one of the Georgia pebbles is roughly 40 percent high magnesium calcite and 60 percent aragonite as opposed to the essentially 100 percent aragonite cement noted by Ginsburg. It is possible that high Mg calcite secreting algae played an important role in cementing the Georgia pebbles. Perhaps the Georgia beach rock was broken up during storms and the individual fragments were then rounded in the surf zone. The highly unstable carbonate mineralogy indicates the pebbles were never subjected to significant subaerial weathering.

The small amounts of phosphorous noted in the oolites may represent an early state of phosphatization by the carbonate replacement mechanisms discussed by Ames (1959). The wide variation in color of individual oolites may represent various early stages of phosphatization. It is difficult however to understand the color variation of oolites in a single sample. That is, if phosphatization is occurring, why is it not occurring at equal rates on all grains? Perhaps the dark grains are surficial sediment constituents, and the less affected grains are found further below the sediment-water interface. Careful core examination should aid in answering this question.

The restricted environment of oolite origin is very useful for precise dating of Pleistocene shorelines. *Crassostrea virginica* shells have been used for this purpose in the Gulf of Mexico (Curray, 1960) and in U. S. Atlantic shelf sediments north of Cape Hatteras (Merril, Emery, and Rubin 1965). Detailed, very careful dating of oolitic material in this area, particularly when combined with oyster dates, should add considerably to our knowledge concerning the recent rise of sea level curve.

nanuscript and offered suggestions and criticisms. Collection of samples and some preliminary work was accomplished on this study while the senior author was a member of the staff of the University of Georgia Marine Institute and Geology department.

## REFERENCES

AMES, L. L., JR., 1959, The genesis of carbonate apatites: Econ. Geology, v. 54, p. 829–841.

CURRAY, J. R., 1960, Sediments and history of Holocene transgression, continental shelf, northwest Gulf of Mexico, *in* Shepard, F. P., Phleger, F. B., and Andel, T. H. van, eds., Recent sediments, northwest Gulf of Mexico: Am. Assoc. Petroleum Geologists, 394 p.

GINSBURG, R. N., 1953, Beachrock in South Florida: Jour. Sedimentary Petrology, v. 23, p. 85–92.

GORSLINE, D. S., 1963, Bottom sediments of the Atlantic shelf and slope off the southern United States: Jour. Geology, v. 71, p. 422–440.

MERRILL, A. S., EMERY, K. O., AND RUBIN, MEYER, 1965, Ancient oyster shells on the Atlantic continental shelf: Science, v. 147, p. 398–400.

NEWELL, N. D., PURDY, E. G., AND IMBRIE, JOHN, 1960, Bahamian oolitic sand: Jour. Geol., v. 68, p. 481–497.

PILKEY, O. H., AND GILES, R. T. (1965), Bottom topography of the Georgia continental shelf: Southeastern Geology, v. 7, p. 15–18.

STETSON, H. C., 1938, The sediments of the continental shelf off the eastern coast of the United States: Massachusetts Inst. Technology and Woods Hole Ocean. Inst., Paper in Phys. Oceanography and Meteorology, v. 5, p. 48.

SUBBA RAO, M., 1964, Some aspects of continental shelf sediments of the east coast of India: Marine Geol. v. 1, p. 59–87.

WILCOXIN, J. A., 1964, Distribution of Foraminifera off the southern Atlantic coast of the United States: Contr. Cushman Found., v. 15, p. 1–24.

# THE ESTUARINE FORMATION OF UNITED STATES ATLANTIC COASTAL PLAIN PHOSPHORITE [1]

## D. R. PEVEAR

### ABSTRACT

Dissolved inorganic phosphorus concentrations in estuaries are commonly high enough to cause phosphatization of calcium carbonate. The large phosphorus values are due to the high productivity of organisms, especially plants. The aerial distribution, stratigraphy, mineralogy, and fossils of the Tertiary Atlantic coastal plain phosphorite support a near-shore, probably estuarine origin for the deposits.

## INTRODUCTION

MANY of the world's phosphorite occurrences can be genetically related to strong marine upwelling. The Tertiary phosphorite deposits of the Atlantic Coastal Plain have many dissimilarities to this type of deposit, as pointed out by Sheldon (27). Cathcart (5) hypothesizes that the Florida deposits are a residuum from the weathering of the slightly phosphatic Hawthorn limestone. Malde (19) believes that the South Carolina phosphorite was formed by replacement of a limestone. Neither author indicates the source of phosphorus or under what conditions original phosphorite formation took place. A new hypothesis is proposed whereby phosphorite forms by replacement of limestone in productive estuarine waters which are distant from major marine upwelling.

## UPWELLING HYPOTHESIS

The concept that sedimentary phosphorite deposits form in areas of upwelling marine waters, first stated by Kazakov (18) and later modified by McKelvey (20), Sheldon (26, 27), and others, offers an attractive explanation for the origin of such deposits. N, P, Si, and $CO_2$ become concentrated (relative to the ocean as a whole) at depths below 500 m in the oceans due to the accumulation and decay of organic materials sinking from the surface (29, 4, 22). Where currents cause these deep waters to be brought to the surface, as on the west coasts of some continents (33), large populations of organisms (15, 24) and deposition of phosphorite and silica may occur (18, 20, 26, 27). The association of phosphorite, chert, and abundant organic matter, commonly observed in phosphorite deposits of diverse geologic age (20, 26), can be accounted for in this way. Additional conditions necessary for phosphorite deposition are (20, 27): shallow water, increase in temperature of upwelling waters on reaching surface or near surface, and low rate of supply of terriginous detritus. Some phosphorites may form in a reducing

[1] Contribution No. 96, from the Marine Institute, Univ. of Georgia, Sapelo Island, Ga.

environment, as evidenced by high amounts of uranium (100–200 ppm) (12, ' '
and the presence of glauconite (23, 27), and pyrite (8, 1).

Upwelling waters and oceanic waters at depths of 500 m and more do
not generally contain more than 3 mg-atoms/meter³ of dissolved inorganic
phosphorus, while near surface waters contain only 1/10 of this amount (4,
22, 24, 33). It should be pointed out, however, that regions of upwelling
are not the only oceanic areas having large concentrations of phosphorus.

## PHOSPHORUS CONCENTRATION IN ESTUARIES

Estuaries, fiords and other near-shore basins commonly contain 1–10 mg-
atoms/m³ of dissolved inorganic phosphorus (22, 25), although such areas may
be remote from oceanic upwelling. Fiords and basins with sills attenuating
outward flow maintain restricted, anaerobic conditions at depth where phos-
phorus and other nutrient elements resulting from decay of organisms accumu-
late (22). Estuaries may serve as "nutrient traps" by virtue of their circu-
lation in the manner described by Redfield (22) and maintain phosphorus
values up to 4 mg-atoms/m³ (22, 25). A mechanism by which estuaries
"trap" phosphorus will be discussed below.

The estuaries of coastal Georgia are among the most productive areas in
the world in terms of grams of dry organic matter per m² per year (25). The
mechanisms maintaining the high productivity are discussed by Schelske and
Odum (25). The most important contributing factor is probably the large
population of marsh grass and benthic algae, which synthesize food for ad-
ditional organisms. Inorganic phosphorus values in the estuarine waters
range from 1–4 mg-atoms/m³ (25), whereas in the nearby Altamaha River
and adjacent ocean only about 0.1 mg-atom/m³ is present (25, 30). It is
evident that the high inorganic phosphorus values in the estuaries are not the
result of influx of similar concentrations from either the ocean or rivers.
The key to the high phosphorus content lies in the high productivity. Most
of the estuarine phosphorus is tied up in the biota of the estuary, especially
*Spartina alterniflora* (marsh grass) and benthic algae (14). Upon death the
organism ultimately decays and the phosphorus is liberated as inorganic phos-
phorus, in which form it can again be utilized by plants and other organisms.
An exchange equilibrium is thus established between inorganic phosphorus
and phosphorus tied up in the tissues of living and dead organisms (32). The
actual rate of exchange, judging from work in other areas (32), is in the
order of a few days.

The biologic exchange mechanism supplies only the concentration that may
be necessary for phosphorite formation. The actual volume of phosphorus
must come from either the rivers or ocean or both. Organisms must not be re-
garded as using up phosphorus to any extent; they merely "trap" it within the
limits of the estuary and use it over and over again. If phosphorus were
regularly removed by a mechanism such as phosphorite formation, it seems
likely that it would be replenished by either river influxes or tidal exchange
with the ocean. Over a period of one million years a typical Georgia estuary
of less than twenty square miles area could produce one half billion tons of

pure phosphorite if all the inorganic phosphorus from the Altamaha River and tidal exchange were precipitated. It is unlikely that all phosphorus entering the estuary would be incorporated into phosphorite. A figure of about 200 million tons, corresponding to a pure phosphorite layer 5 m thick over the whole estuary, seems more realistic.

## ADDITIONAL CONDITIONS

One now comes to the question as to why phosphorite is not presently precipitating in Georgia estuaries. Additional conditions for phosphorite formation must be specified. The experimental work of Ames (2) indicates that replacement of calicum carbonate is very likely the only manner in which carbonate fluor-apatite, the essential component of all marine phosphorites (3), can form in sea water. Ames further states that, under the conditions of pH and $CaCO_3$ saturation in normal sea water, concentrations of less than 0.1 ppm phosphate (1 mg-atom/m$^3$) are not capable of replacing carbonate. This value may be somewhat higher in sea water due to the effects of possible complexing or interionic attraction, although Ames' work indicates that the replacement reaction is little influenced by large concentrations of alkalies.

Phosphorite is not presently forming in Georgia estuaries because there is virtually no $CaCO_3$ present. The sediments consist of quartz sand and montmorillonite-kaolinite mud. Calcareous shells are soon dissolved below the interface of the muds where more or less acid reducing conditions prevail.

Phosphorite is not forming in the $CaCO_3$-rich South Florida and Bahamian regions because the phosphorous concentration of these waters is below the critical value given by Ames. On the Andros bank the inorganic phosphorus values average about 0.1–0.3 mg-atoms/m$^3$ (7, 31).

Phosphorite has been described on the Portales Terrace south of the Florida Keys (10, 16). The terrace is composed of Tertiary limestones that may be undergoing phosphatization although it is equally possible that the phosphorite is of Tertiary age. Phosphorus values given by Cloud (7) for the Gulf Stream in South Florida may be high enough to cause some phosphatization of nearby $CaCO_3$. This would account for the material on the Portales Terrace and the high $P_2O_5$ values (up to 6%) given by Gorsline (11) for sediments off the S.E. coast of Florida.

Phosphorite deposition could take place following a period of carbonate deposition. A cooling climatic trend would result in a withdrawal of $CaCO_3$ precipitating conditions and an increase in productivity of estuarine waters. If the concentration of phosphorus rose above 1 mg-atom/m$^3$ the existing lime muds would be converted to phosphorite. Reducing conditions might exist in these muds as they do in muds of modern estuaries. Phosphorous values in the interstitial water below the interface of the muds could be considerably higher than in the overlying water (17). The high productivity of the estuary would result in the muds having appreciable organic content. Were $CaCO_3$ and phosphorite forming conditions to exist simultaneously a phosphatic limestone might result. A slow rate of supply of terrigenous detritus must also obtain in order that the slowly accumulating chemical

sediments not be diluted. A more general but somewhat similar argument to that given above is presented by Charles (6).

### EVIDENCE FROM DEPOSITS

Turning to the Tertiary Atlantic coastal plain deposits (1, 5, 13, 19, 23) we will look for evidence that these phosphorites were formed by the process outlined above. The existence of phosphatic material of Miocene age in a more or less continuous band from Maryland to South Florida is evidence of interrelation between the three important mining areas in Florida, South Carolina and North Carolina. Most of these deposits have been extensively reworked into Miocene, Pliocene, or Pleistocene detrital sediments obscuring evidence of actual phosphorite formation.

Although phosphorite is ubiquitous on the coastal plain large concentrations are confined to several relatively small areas. This suggests that distribution may have been controlled by geography with concentrations accumulating in small coastal basins or estuaries.

In some deposits fossils of land vertebrates and marine animals are found intermixed. Bones of the manatee, a brackish water seal-like mammal, are particularly common in the Florida deposits. If these fossils are indeed related to the phosphorite, and not deposited during later reworking, then they indicate a very nearshore, possibly estuarine, environment.

Malde (19) describes a lime marl in South Carolina that passes upward into an extensively phosphatized surface. He believes this material to be the original source of phosphorite that has been reworked into Pleistocene sand and pebble deposits. The writer has seen similar phosphatized surfaces in the deposits of South Florida. Such surfaces are rarely mentioned in the literature and are probably not often preserved. The majority of the phosphorite occurs as nodules, pebbles, and sand grains admixed with quartz sand and montmorillontic clay (5, 19, 23). Alternation of phosphatized beds, which require a low rate of supply of terriginous detritus, with beds of reworked phosphorite containing sand and clay of terriginous derivation within a short stratigraphic interval requires either 1) rapid oscillation of conditions, 2) that the short stratigraphic interval represents a long time interval and is thus a condensed section as suggested by Sheldon (27) for some phosphorites, or 3) a combination of the two factors.

### MODEL OUTLINE OF HISTORY OF DEPOSITS

The stratigraphy and structure of the Atlantic coastal plain and continental shelf indicate that the gross depositional environment on this rather stable shelf, in terms of major oceanic currents and relative depths, has not changed appreciably since Cretaceous time (28). It seems justified, therefore, to envision sedimentation during Miocene time as having occurred on a coast not dissimilar to that of modern Georgia, with a wide shelf and shoreline embayed by many estuaries.

During a period of warm climate and relatively low relief limey sediments

accumulated within the sheltered confines of productive coastal estuaries on a broad continental shelf. Cooling climatic conditions resulted in a slackening or withdrawal of limestone-forming conditions and a possible slight increase in productivity due to increased $CO_2$ solubility. High productivity, especially of marsh grass and benthic algae, raised inorganic phosphorus concentrations to a point where lime mud was replaced by phosphorite. During a period of 60,000 years one foot of phosphorite was produced over most all the estuaries. Small shelf instabilities resulted in significant changes of sea level on the shallow shelf causing the surf zone to transgress over the estuary breaking up and somewhat redistributing the phosphorite. The process of formation and breaking up of the phosphorite layer occurred repeatedly during Miocene time. Subsequently, during Pliocene and Pleistocene time, continued transgressions and regressions reworked phosphorite pebbles and grains into sediments of considerable aerial extent.

Present continental shelf sediments contain disseminated phosphorite sand grains of probable Miocene age (21).

## SUGGESTIONS FOR EXPLORATION

On shallow rather stable shelves, where this type of phosphorite occurs, transgressions and regressions of the sea result in considerable reworking of sedimentary materials, and detrital phosphorite is likely to become widely distributed in sediments formed subsequent to the phosphorite. In attempting to locate new deposits, tracing the source of transported phosphorite should lead to a major concentration near the original place of formation. Finely disseminated grains might be far from the original source but larger pebbles and cobbles indicate that the source is not far removed. The recognition of minor amounts (1 or 2%) of phosphorite grains in sediments could be a useful tool for exploration. In this regard the phosphorite pebbles in the Brightseat Formation of Maryland (1) may have been derived from a nearby but as yet unknown source area. As this type of phosphorite is believed to form by replacement of limestone or lime mud, deposits should always occur adjacent to or above limestone or marl.

DEPARTMENT OF GEOLOGY,
     THE UNIVERSITY OF MONTANA,
         MISSOULA, MONTANA,
            *June 4, 1965*

## REFERENCES

1. Adams, John K., Groot, Johan J., and Hiller, N. William, Jr., 1961, Phosphatic pebbles from the Brightseat formation of Maryland: Jour. Sed. Pet., v. 31, p. 546–562.
2. Ames, L. L., Jr., 1959, The genesis of carbonate apatites: ECON. GEOL., v. 54, p. 829–841.
3. Altschuler, Z. S., Cisney, E. A., and Barlow, I. H., 1953, X-ray evidence of the nature of carbonate-apatite: Internat. Geol. Cong., 19th, Algiers 1952, Comptes rendus, sec. 11, pt. 11, p. 9 (abstract).
4. Barnes, H., 1957, Nutrient elements. In: J. W. Hedgpeth (editor), Treatise on marine ecology and paleoecology, v. 1, Geol. Soc. America Memoir 67, p. 297–344.

5. Cathcart, J. B., Blade, L. V., Davidson, D. F., and Ketner, K. B., 1953, The geology of the Florida land pebble phosphate deposits: Internat. Geol. Cong., 19th, Comptes rendus, sec. 11, pt. 11, p. 77–91.
6. Charles, Georges, 1953, Sur l'origine des gisements de phosphates de chaux sedimentaires: Internat. Geol. Cong., 19th, Comptes rendus, sec. 11, pt. 11, p. 163–184.
7. Cloud, Preston E., Jr., 1962, Environment of calcium carbonate deposition west of Andros Island, Bahamas: U. S. Geol. Surv. Prof. Paper 350, 138 p.
8. Galliher, E. W., 1931, Collophane from Miocene brown shales of California: Bull. Am. Assoc. Petroleum Geol., v. 15, p. 257–269.
9. Goldberg, E. D., 1963, The oceans as a chemical system. In: M. N. Hill (editor), The Sea, v. 2. Interscience, New York, p. 3–25.
10. Gorsline, D. S., and Milligan, D. B., 1963, Phosphatic deposits along the margin of the Pourtales Terrace, Florida: Deep-Sea Res., v. 10, p. 259–262.
11. Gorsline, D. S., 1963, Bottom sediments of the Atlantic shelf and slope off the southern United States: Jour. Geol., v. 71, p. 422–440.
12. Habashi, Fathi, 1962, Correlation between the uranium content of marine phosphates and other rock constituents: ECON. GEOL., v. 57, p. 1081–1084.
13. Herrick, Stephen M., 1961, Well logs of the coastal plain of Georgia: Georgia Geol. Survey Bull. 70, 462 p.
14. Johannes, Robert, 1964, Oral communication.
15. Johnson, Martin W., 1957, Plankton. In: J. W. Hedgpeth (editor), Treatise on marine ecology and paleoecology, v. 1, Geol. Soc. America Memoir 67, p. 443–460.
16. Jordan, G. F., Malloy, R. J., and Kofoed, J. W., 1964, Bathymetry and geology of Pourtales Terrace, Florida: Marine Geol., v. 1, p. 259–287.
17. Kaplan, I. R., and Rittenberg, S. C., 1963, Basin sedimentation and diagenesis. In: M. N. Hill (editor), The Sea, v. 3. Interscience, New York, p. 583–619.
18. Kazakov, A. V., 1937, The phosphorite facies and the genesis of phosphorites. In Geological investigations of agricultural ores, USSR: Leningrad Sci. Inst. Fertilizers and Insecto-Fungicides Trans. (USSR), no. 142, p. 95–113.
19. Malde, Harold E., 1959, Geology of the Charleston Phosphate area, South Carolina: U. S. Geol. Surv. Bull. 1079, 105 p.
20. McKelvey, V. E., Swanson, R. W., and Sheldon, R. P., 1953, The Permean phosphorite deposits of western United States: Internat. Geol. Cong., 19th, Comptes rendus, sec. 11, pt. 11, p. 45–64.
21. Pevear, D. R., and Pilkey, Orrin H., in preparation, Phosphorite on the Georgia continental shelf.
22. Redfield, A. C., Ketchum, B. H., and Richards, F. A., 1963, The influence of organisms on the composition of sea-water. In: M. N. Hill (editor), The Sea, v. 2. Interscience, New York, p. 26–77.
23. Rooney, Thomas P., and Kerr, Paul F., 1964, Mineralogy of North Carolina phosphorite. Program—Geol. Soc. America Ann. Meeting, p. 165–166 (abstract).
24. Ryther, John H., 1963, Geographic variations in productivity. In: M. N. Hill (editor), The Sea, v. 2. Interscience, New York, p. 347–380.
25. Schelske, Claire L., and Odum, Eugene P., 1961, Mechanisms maintaining high productivity in Georgia estuaries: Proceedings of the Gulf and Caribbean Fisheries Inst., 14th Ann. Session, p. 75–80.
26. Sheldon, Richard P., 1964, Paleolatitudinal and paleographic distribution of phosphorite: U. S. Geol. Surv. Prof. Paper 501-C, p. C106–C113.
27. Sheldon, Richard P., 1964, Exploration for phosphorite in Turkey—a case history: ECON. GEOL., v. 59, p. 1159–1175.
28. Stetson, H. C., 1938, The sediments of the continental shelf off the eastern coast of the United States: Papers in Phys. Oceanography and Meteorology, MIT, v. 5, no. 4, 48 p.
29. Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., 1946, The oceans, their physics, chemistry and general biology: New York, Prentice-Hall Inc., 1087 p.
30. Thomas, James P., 1964, Oral communication.
31. Traganza, E. D., 1964, Oral communication.
32. Watt, W. D., and Hays, F. R., 1963, Tracer study of the phosphorus cycle in sea water: Limnology and Oceanography, v. 8, p. 276–285.
33. Wooster, W. S., and Reid, J. L., 1963, Eastern boundary currents. In: The Sea, v. 2. Interscience, New York, p. 253–280.

DAVID R. PEVEAR   *Dept. Geology, University of Montana, Missoula, Montana*
ORRIN H. PILKEY   *Dept. Geology, Duke University, Durham, North Carolina*

# Phosphorite in Georgia Continental Shelf Sediments

**Abstract:** Rounded, polished phosphorite sand grains in Georgia continental shelf, beach, and estuarine sediments average 1 per cent of the total sediment. An amber and a black variety are present everywhere except in estuaries where only the black is present. The black color is due primarily to inclusions of pyrite and carbonaceous matter. The lack of amber grains in estuaries may reflect reducing conditions favoring pyrite formation. The phosphorite and quartz fractions of most samples are similar in size. This plus the high polish on phosphorite grains (which tumbling-barrel experiments show can be due to abrasion) indicate a probable detrital origin of the phosphorite.

Shelf phosphorite must have been derived from Pleistocene river sources or outcropping phosphate-rich ancient sediments on the shelf, for present-day rivers are not carrying this material. The presence of phosphorite in beaches and estuaries indicates that much of these sands are derived by landward transport of sediments from the continental shelf.

## CONTENTS

## INTRODUCTION

The phosphorite content of Georgia continental shelf, beach, and estuarine sediments has been investigated in one of a series of studies being carried out to elucidate the history of sedimentation on the continental shelf off the Southeastern United States. The purpose of the present study is to determine the nature, distribution, abundance, and genesis of shallow-water Atlantic shelf phosphorite.

Various aspects of sedimentation in this area have been reported by Stetson (1938), Gorsline (1963), Uchupi (1963), and Pilkey (1963; 1964). Most of the Georgia shelf is covered by moderately sorted relict (Pleistocene) quartz sand containing appreciable amounts of calcareous shell material. A distinct near-shore band of fine sand and silt 10–12 miles wide may represent modern deposition. The continental slope limits the outer edge of the 80-mile-wide Georgia shelf at depths ranging from 180 to 250 feet. The deepest samples utilized in this study are from about 500 feet.

Emery (1960) summarized much of the available information concerning phosphorites on

the sea floor. Previous studies have been concerned with greater concentrations of phosphorite than reported here. Gorsline (1963) noted the presence of minor amounts of sand-sized phosphorite grains within the study area. Em-

and along with Dr. Donald Winston and Dr. Donn S. Gorsline critically reviewed the manuscript. Mr. Stan Riggs offered several valuable suggestions and comments at the beginning of the study.
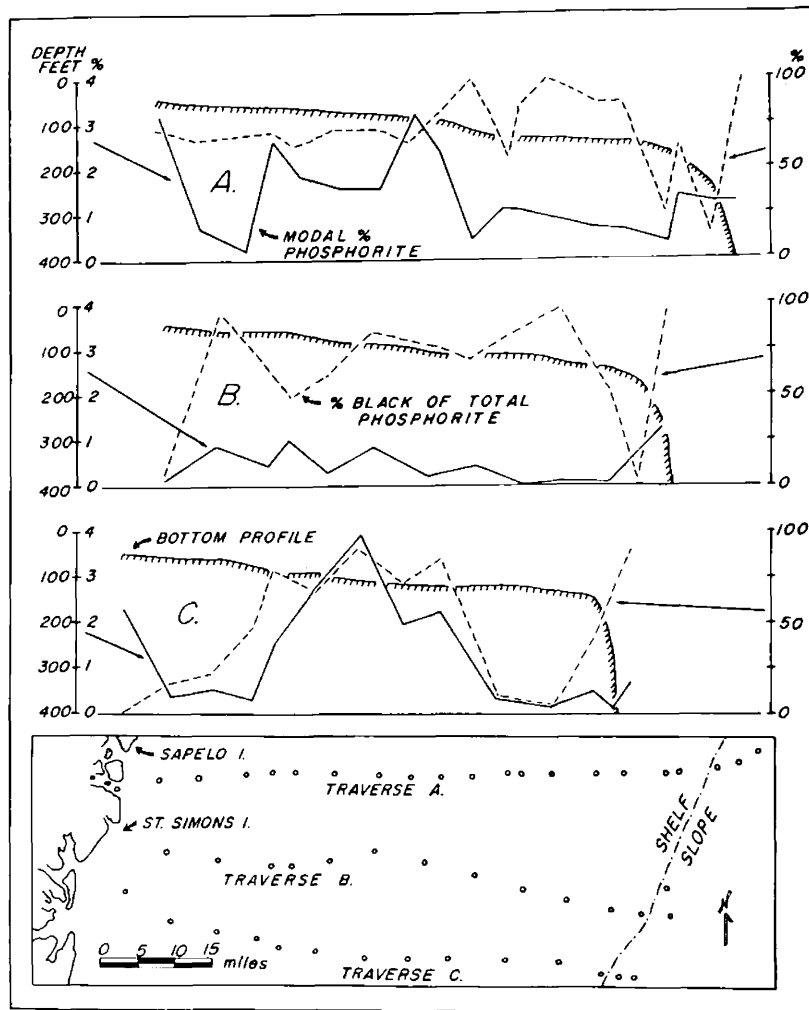


Figure 1.    Plots of the percentage of phosphorite grains of total sediment and percentage of black grains of the total phosphorite fraction *versus* distance from shore. The hachured line is a topographic profile of the shelf. The map at the bottom of the figure shows the sample locations. *Refer to* Figure 2 for index map.

cry (personal communication) has observed large phosphorite nodules on the inner Blake Plateau, just seaward from the study area.

## METHODS

Shelf-sediment samples were collected with a Pierce box dredge. Sample locations are shown in Figure 1. Estuarine samples (Fig. 2) were collected with a small Seki sampler.

Median grain sizes and sorting of both acid-insoluble residues and total samples were determined using standard techniques. The amount and size distribution of the phosphorite

were determined by counting individual grains in lakeside slide mounts of separate sieve fractions. Phosphorite size distributions were calculated by weighting the proportion of phosphorite present in each size fraction by an amount based on the relative abundance of that

Plastic-mounted thin sections were made of phosphorite grains so that internal structures could be observed. To determine the effect of abrasion on phosphorite grains, a tumbling barrel was devised from a rotating dark-room print dryer.
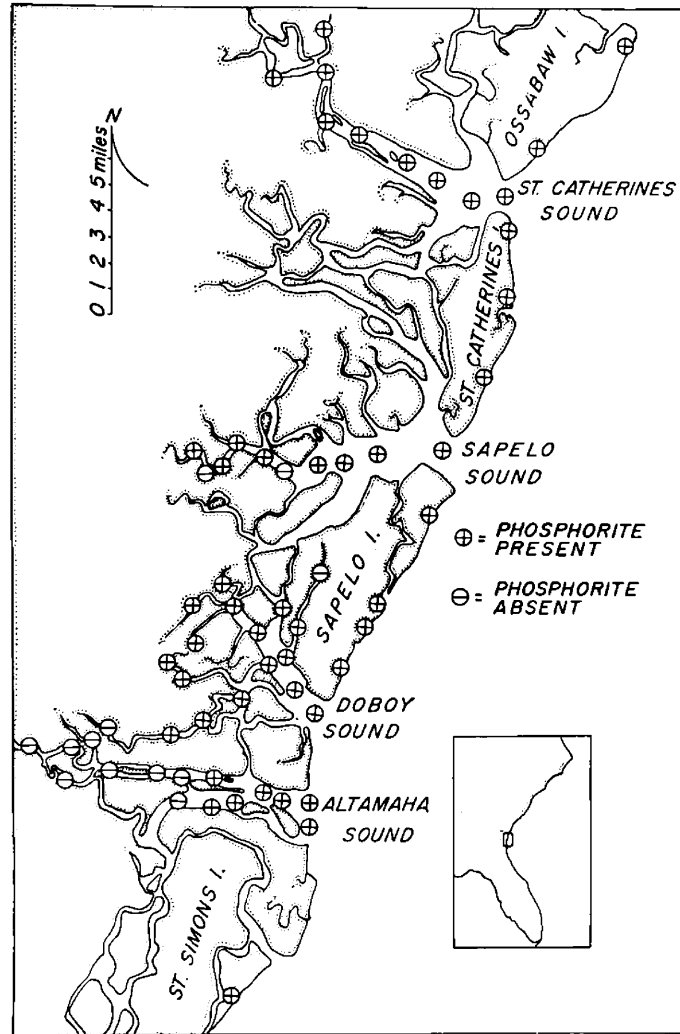


Figure 2.   Map showing Georgia beach and estuarine-sample locations and also the presence or absence of phosphorite in the sediment.

size fraction in the total untreated sample. Phosphatic grains were identified by a standard spot test solution of ammonium molybdate in dilute nitric acid. This solution produces slow effervescence (relative to calcite) and a deep-yellow precipitate. Without the spot test, certain types of phosphorite grains were difficult to distinguish from detrital limestone grains or heavy minerals, such as magnetite and illmenite.

## RESULTS

### Grain Size

Most of the phosphorite of Georgia shelf, estuarine, and beach sediments is sand-sized; some is silt-sized. The presence of clay-size phosphorite was not ascertained. (Griffin, 1963, has reported a phosphate mineral from the clay fraction of a Florida beach sand.) The largest

phosphatic grain observed is about 1.5 cm long.

In any given sample, the median grain size of the phosphorite closely approximates that of the acid insoluble residue (quartz grains). This can be seen in Figure 3. The phosphorite median diameter tends to be slightly less than that of quartz in a given sample (as can be seen in Fig. 3), probably because phosphorite has a slightly higher specific gravity. The relationship between quartz grain size and that of the phosphorite fraction can be observed in beach and estuarine samples as well as open-shelf sediments.

*Sorting*

Sorting (Trask) for both phosphorite and quartz components is similar and shows little variation in samples examined. On the shelf, sorting is moderate (1.35–1.85) except near shore where the sands are moderately well sorted (1.20–1.35). Beach sands are moderately well sorted.

*Physical Appearance*

Phosphorite grains are typically polished and well rounded (Pl. 1, fig. 1). The majority show no indication of direct organic origin although a quantitatively unimportant number of bone fragments and teeth are present. Figure 2 of Plate 1 illustrates the unique appearance of bone in thin section.

Two distinct color types of phosphorite can be distinguished with little gradation between them. These are a black to dark-brown opaque variety, and a more or less translucent, amber to yellow-brown variety. Both varieties are optically isotropic. The black opaque grains contain abundant inclusions of a metallic mineral (probably pyrite), illitic clay, and organic matter. The pyrite is probably largely responsible for the dark color although carbonaceous organic matter also plays a role. Pyrite in similar phosphorite grains has been observed by Galliher (1931) and Adams and others (1961). In some grains, the inclusions are evenly distributed, whereas in others, they are distinctly segregated in the interior or at the grain rim (Pl. 1, figs. 3, 4). The variable nature of inclusion distribution within single grains probably reflects a variety of complex single grain histories. Amber grains contain free iron oxide but no inclusions. Many large grains (up to 1.5 cm) contain sand-size quartz and foraminifera tests.

Most of the phosphorite grains have highly polished surfaces. This polish has been attributed to chemical precipitation (Dietz and

others, 1942; Uchupi, 1961), but the tumbling-barrel experiments of this study indicate that this polish can also be due to abrasion. Quartz sand containing phosphorite was placed in two 1-liter jars and allowed to roll back and forth for several days with a relatively gentle motion; One jar contained a freshly crushed phosphorite nodule from a commercial Miocene deposit near Bartow, Florida, admixed with quartz sand. The second jar contained slightly phosphatic sand from the Georgia shelf which was unaltered except that the surface of the phosphorite grains had been dulled by brief treatment with dilute hydrochloric acid. Observations during several stages of tumbling indicate that the degree of polish is directly proportional to tumbling time.

X-ray diffraction studies of the phosphorite indicate that both the amber and black varieties are carbonate-fluorapatite. Diffraction patterns of black grains indicate the presence of pyrite and illitic clay in the insoluble residue. Diffraction patterns of Tertiary coastal plain phosphorite from Florida and South Carolina (Malde, 1959) are identical to those of this study.

*Distribution*

Figure 1 shows the abundance of phosphorite on the shelf plotted as a function of distance from shore. The phosphorite content of Georgia shelf sediments averages 1.1 per cent and ranges between 0.0 per cent (one sample) and 3.9 per cent. Figure 1 shows that no consistent trends of phosphorite grain abundance with distance from shore are present. It also shows that the percentage of black grains of the total phosphate fraction shows no particular trend other than a slight predominance over amber grains.

Phosphorite grains in Georgia beaches (nine samples counted) range in abundance from 0.3 per cent to 4.1 per cent and average 1.4 per cent. In local estuaries (11 samples counted), the abundance ranges between 0.1 per cent and 4.9 per cent and averages 1.1 per cent.

The proportion of black to brown grains in beach sands is similar to that of shelf sediments (Fig. 1). However, amber phosphorite grains are strikingly absent from estuarine sediments. This does not necessarily indicate a unique source or type of phosphorite but rather may reflect the presence of estuarine reducing conditions causing formation of pyrite. Free iron oxide in the amber grains may provide iron for pyrite formation; whereas, sulfur in sulfide form is abundant below the interface of estuarine
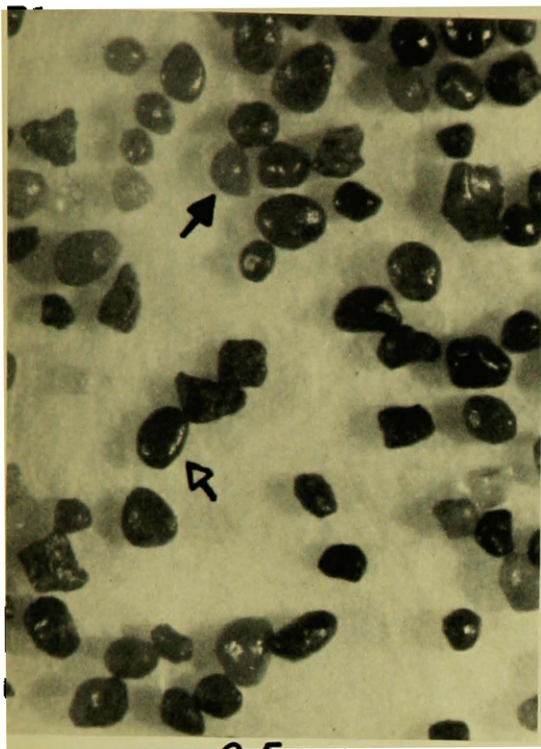
Figure 1.  Photograph of grains in sediment; unfilled arrow — black grain, filled arrow — amber grain



Figure 2.  Bone fragment in thin section; note the unique structure (osteoblasts)



Figure 3.  Phosphorite grains in thin section, illustrating varied distribution of inclusions within individual grains
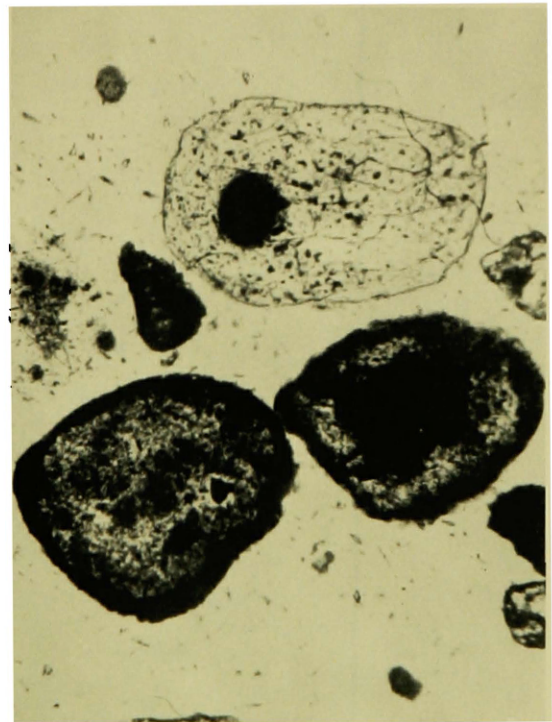


Figure 4.  Same as Figure 3

PHOTOMICROGRAPHS OF PHOSPHORITE GRAINS FROM CONTINENTAL SHELF, BEACH, AND ESTUARINE SEDIMENTS OF GEORGIA
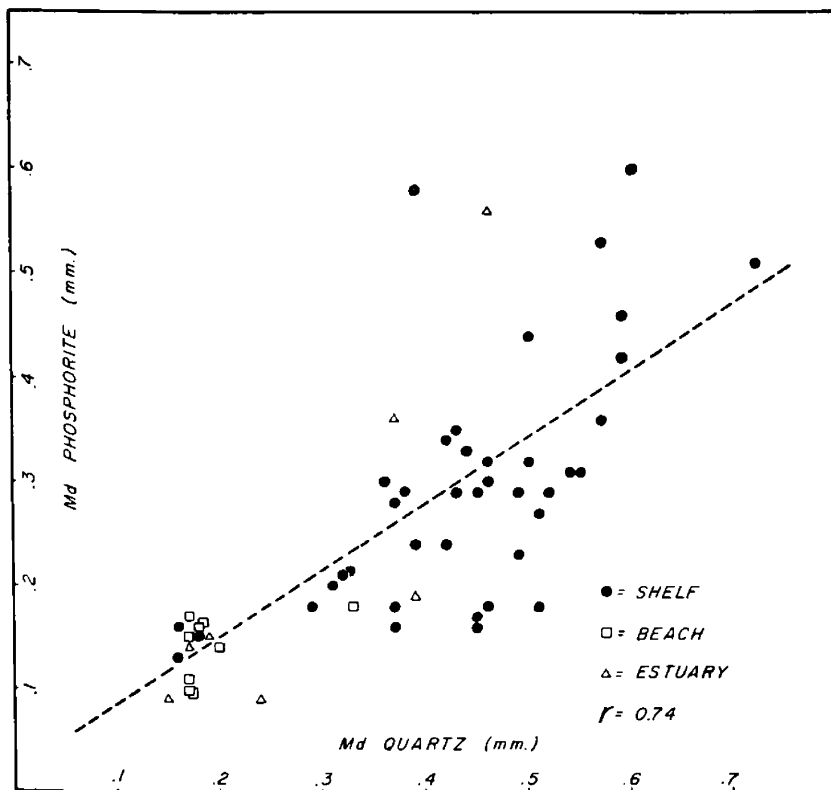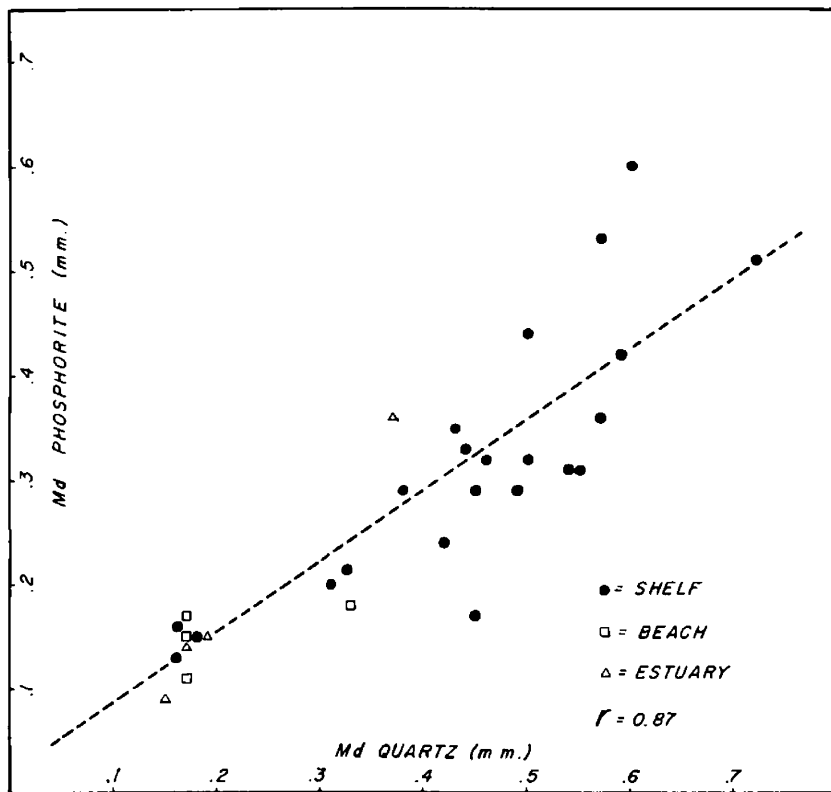
Figure 3.   Plots of median grain size of phosphorite *versus* median grain size of the acid insoluble residue (quartz) of Georgia shelf, estuarine, and beach sediments. Figure 3A is a plot of all the data except those few samples containing less than 0.25 per cent phosphorite. Figure 3B is a plot of only those samples containing more than 1 per cent phosphorite, upon which a more accurate size determination of the phosphorite was possible.

muds. It is possible that organic matter, such as hydrocarbons, may be converted to carbonaceous inclusions in this environment. The presence of amber grains in shelf and beach sediments indicates that these grains, during their past history, were not subjected to reducing

center of the study area, was particularly heavily sampled. A number of other rivers in North and South Carolina were also sampled (Fig. 4) and are discussed in a later section. Other than river samples, the only sands that lacked phosphorite were a number from Altamaha Sound
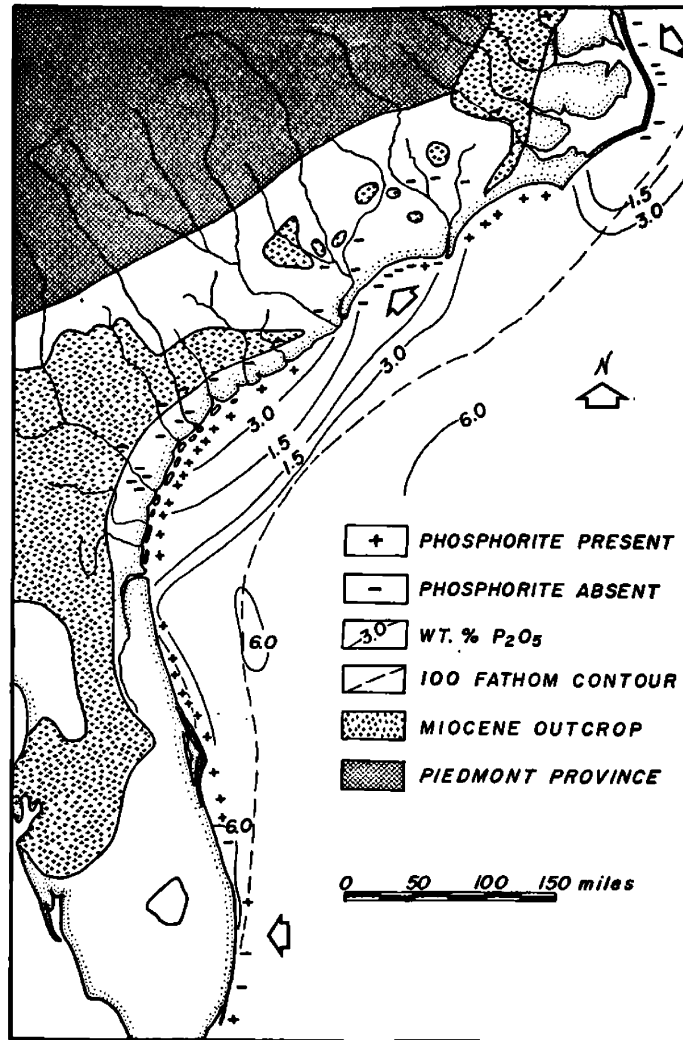
Figure 4. Map showing the presence or absence of phosphorite in beaches and rivers of the southern U. S. Atlantic Coast. Also shown are the P₂O₅ content of shelf sediments (Gorsline, 1963), the location of Miocene outcrops, and the Piedmont metamorphic province.

conditions similar to those in modern estuaries. Alternatively, the pyrite may have been subsequently oxidized.

The Savannah, Ogeechee, and Altamaha river beds of Georgia were sampled; virtually no phosphorite was observed in these sands. The Altamaha River, which is in the approximate

and two from Sapelo Sound. Figure 2 shows the location of the estuarine samples that were studied.

DISCUSSION

The phosphorite observed in Georgia beach, shelf, and estuarine sediments is believed to be

detrital. The principal supporting evidence is the close relationship between the median grain size of the acid insoluble residue (essentially quartz grains) and that of the phosphorite fraction. There is no reason to expect any such relationship if phosphorite grains are *in situ* chemical precipitates. Rather, the similarity of phosphorite and quartz grain sizes must reflect similar recent histories of transportation. Furthermore the high surface polish on individual grains may well be direct evidence of a long period of abrasion. Phosphorite from locally derived bone or teeth is of little importance.

Phosphorite, often occurring in grains physically identical to those in modern sediments, is abundant in certain coastal plain rocks, particularly those of Miocene age. These phosphorites have been described by Mansfield (1940), Malde (1959), Adams and others (1961), Herrick (1961), and Rooney and Kerr (1965). The sand-size polished grains in these sediments have been described as "reworked" by most authors.

The phosphorite in modern Georgia shelf sediments is obviously not being contributed in significant amounts by present-day rivers. It was most probably eroded from Miocene and other coastal plain sediments by rivers which had increased gradients during lowered sea levels of the Pleistocene. Much evidence, such as coarse grain size, shallow-water shells at depth, and oölites near the shelf edge, indicates a Pleistocene origin of most of the Georgia shelf sediment. Gorsline (1963) suggested that Miocene sediments cropping out on the shelf could be a source of phosphorite. Strata of this age are known to underlie the shelf at a relatively shallow depth (Wait, 1962; Antoine and Henry, 1965; JOIDES, 1965). Miocene sediments also crop out in a deep portion of Sapelo Sound (Darby and Hoyt, 1964) within the study area. This and other outcrops may be contributing small amounts of phosphorite locally.

The fact that shelf, beach, and estuarine sediments all contain phosphorite whereas the nearby rivers do not indicates that the presence or absence of phosphorite may be a valuable aid in tracing sediment sources. For example, using the phosphorite criterion, one may deduce that the Altamaha River is not an important source of sand-size sediment to near-shore areas or even nearby beaches. In fact, judging from the distribution of phosphorite in Altamaha Sound at the mouth of the Altamaha River (Fig. 2), the river sands dominate only in the inner half of the sound. In the outer half of Altamaha Sound as well as the whole of Doboy, Sapelo, and St. Catherine's sounds, most of the sand-size material is very likely derived from the shelf. No rivers of consequence empty into the latter three sounds. The two locations in Sapelo Sound which lack phosphorite (Fig. 2) are both in the vicinity of actively eroding Pleistocene barriers, the sands from which are nonphosphatic.

Beach and river sands were collected between Cape Hatteras, North Carolina, and Miami Beach, Florida, to obtain a regional interpretation for the origin of beach sands of the Southern United States. Figure 4 illustrates the results of these observations and also shows the location of Miocene outcrops on the Atlantic coastal plain and the total $P_2O_5$ content of adjacent continental shelf and slope sediments (*from* Gorsline, 1963). The $P_2O_5$ content reflects phosphorite grains, for the most part, but is also affected by the amount of organic matter present. The $P_2O_5$ isopleth lines are based on a very limited number of samples.

Three broad areas were observed wherein phosphorite is absent or occurs sporadically in the beach sediments (*see* arrows on Fig. 4). These are (1) north of Cape Hatteras (shown by the northernmost arrow), (2) south of Cape Fear, and (3) southern Florida. Cape Fear and southern Florida are relatively far from potentially eroding Miocene outcrops. The Cape Hatteras and Cape Fear areas have corresponding $P_2O_5$ lows in the adjacent shelf sediments, but the $P_2O_5$ data may be too sketchy for meaningful correlations of this sort.

None of the somewhat limited number of river samples contained phosphorite with the one possible exception of the Edisto River in South Carolina. As a general conclusion, it appears that any sediments being contributed to the marine environment by rivers of this entire area are nonphosphatic. It follows that the phosphatic beach sands shown in Figure 4 must have been derived at least in part from continental shelf sources. The source of the beach sands in the three nonphosphatic areas cannot be determined with the available data. It is possible that these sands are also derived from the adjacent shelf, the sediments of which may not contain phosphorite; further shelf sampling will be needed to verify this.

## CONCLUSIONS

(1) Sand-size, rounded, polished, phosphorite grains constitute about 1 per cent of Georgia

continental shelf, beach, and estuarine sediments.

(2) An amber and a black variety of phosphorite are present. The black color is due to the presence of pyrite and carbonaceous matter. In shelf and beach sediments, the black grains are typically slightly more abundant than the amber. In estuarine sediments, the amber variety is absent. The amber may have been converted to black by pyrite formation in the reducing estuarine environment.

(3) Tumbling-barrel experiments indicate that the polished surface of phosphorite grains can be caused by abrasion.

(4) In any given sample, the median size of phosphorite grains closely approximates the median grain size for the acid insoluble residue (quartz grains). This and the polished nature of the grains indicate a probable detrital origin for the phosphorite.

(5) Modern rivers are not contributing sig-nificant amounts of phosphorite to the marine environment. Shelf phosphorite must have been derived either from Pleistocene rivers or from outcropping phosphatic ancient sediments on the shelf.

(6) Phosphorite-free sediments from the Altamaha River, the largest river of the South-eastern Atlantic United States in terms of annual mean discharge, are present only in the inner half of the Altamaha Sound. Nearby beach sands and the estuarine sands in the outer half of Altamaha Sound, as well as the sands in adjacent sounds, are apparently derived by land-ward transport of sands from the continental shelf.

(7) Observations on a limited number of beach and river samples from the entire South-ern Atlantic United States indicate that many of the beach sands over this entire area are de-rived from nonriver sources, probably from the adjacent shelf.

## REFERENCES CITED

Adams, John K., Groot, Johan J., and Hiller, N. William, Jr., 1961, Phosphatic pebbles from the Bright-scat formation of Maryland: Jour. Sed. Petrology, v. 31, p. 546–552

Antoine, John W., and Henry, Vernon J., 1965, Seismic refraction study of shallow parts of the conti-nental shelf off the Georgia coast: Am. Assoc. Petroleum Geologists Bull., v. 49, p. 601–609

Darby, David G., and Hoyt, John H., 1964, An upper Miocene fauna dredged from tidal channels of Coastal Georgia: Jour. Paleontology, v. 38, p. 67–73

Dietz, R. S., Emery, K. O., and Shepard, F. P., 1942, Phosphorite deposits on the sea floor off southern California: Geol. Soc. America Bull., v. 53, p. 815–848

Emery, K. O., 1960, The sea off southern California: New York, John Wiley and Sons, 366 p.

Galliher, E. W., 1931, Collophane from Miocene brown shales of California: Am. Assoc. Petroleum Geologists Bull., v. 15, p. 257–269

Gorsline, Donn S., 1963, Bottom sediments of the Atlantic shelf and slope off the southern United States: Jour. Geology, v. 71, p. 422–440

Griffin, George M., 1963, Occurrence of talc in the clay fractions from beach sands of the Gulf of Mexico: Jour. Sed. Petrology, v. 71, p. 231–233

Herrick, Stephen M., 1961, Well logs of the coastal plain of Georgia: Ga. Geol. Survey Bull. 70, 462 p.

Joint Oceanographic Institutions, Deep Earth Sampling Program (JOIDES), 1965, Ocean drilling on the continental margin: Science, v. 150, p. 709–716

Malde, Harold E., 1959, Geology of the Charleston Phosphate Area, South Carolina: U. S. Geol. Survey Bull. 1079, 105 p.

Mansfield, G. R., 1940, Phosphate deposits of the United States: Econ. Geology, v. 35, p. 405–429

Pilkey, O. H., 1963, Heavy minerals of the U. S. south Atlantic shelf and slope: Geol. Soc. America Bull., v. 74, p. 641–648

—— 1964, The size distribution and mineralogy of the carbonate fraction of United States south Atlantic shelf and upper slope sediments: Marine Geology, v. 2, p. 121–136

Rooney, Thomas P., and Kerr, Paul F., 1965, Mineralogy of North Carolina phosphorite, p. 165–166 in The Geological Society of America, Abstracts for 1964: Geol. Soc. America Special Paper 82, 400 p.

Stetson, H. C., 1938, The sediments of the continental shelf off the eastern coast of the United States: Mass. Inst. Technology Papers in Physical Oceanography and Meteorology, v. 5, no. 4, p. 48

**Uchupi, E.,** 1961, Submarine geology of the Santa Rosa-Cortez Ridge: Jour. Sed. Petrology, v. 31, p. 534–545

—— 1963, Sediments on the Continental Margin off Eastern United States: U. S. Geol. Survey Prof. Paper 475-C, Art. 94, p. 132–137

**Wait, Robert L.,** 1962, Interim Report on test drilling and water sampling in the Brunswick area, Glynn County, Georgia: Ga. State Div. Conserv. Inf. Circ. 23

APPENDIX: Tables of the Median Diameters of Quartz Sand (MdQ) (Insoluble Residue) and Corresponding Phosphorite (MdP), in Millimeters, and Modal Per Cent Phosphorite in the Total Sample (Per Cent P) for Georgia Shelf, Beach, and Estuarine Sediments

**Shelf**

Sample locations on Figure 1, West to East.

| | Traverse A | | | | Traverse B | | | | Traverse C | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | MdP | MdQ | Per cent P | | MdP | MdQ | Per cent P | | MdP | MdQ | Per cent P |
| 1. | 0.13 | 0.16 | 3.2 | 1. | 0.17 | 0.37 | 0.1 | 1. | 0.15 | 0.17 | 2.3 |
| 2. | 0.58 | 0.39 | 0.7 | 2. | 0.16 | 0.37 | 0.9 | 2. | 0.18 | 0.29 | 0.3 |
| 3. | 0.19 | 0.70 | 0.2 | 3. | 0.16 | 0.45 | 0.4 | 3. | 0.18 | 0.37 | 0.5 |
| 4. | 0.20 | 0.31 | 2.6 | 4. | 0.17 | 0.45 | 1.0 | 4. | 0.18 | 0.51 | 0.3 |
| 5. | 0.31 | 0.54 | 1.9 | 5. | 0.24 | 0.39 | 0.3 | 5. | 0.21 | 0.32 | 1.6 |
| 6. | 0.42 | 0.59 | 1.7 | 6. | 0.32 | 0.50 | 0.9 | 6. | 0.29 | 0.45 | 2.7 |
| 7. | 0.29 | 0.49 | 1.6 | 7. | 0.34 | 0.67 | 0.2 | 7. | 0.51 | 0.72 | 3.9 |
| 8. | 0.44 | 0.50 | 3.2 | 8. | 0.29 | 0.43 | 0.4 | 8. | 0.31 | 0.55 | 1.9 |
| 9. | 0.35 | 0.43 | 2.4 | 9. | . . | 0.56 | 0.0 | 9. | 0.36 | 0.57 | 2.2 |
| 10. | 0.23 | 0.49 | 0.4 | 10. | 0.18 | 0.60 | 0.1 | 10. | 0.29 | 0.52 | 0.3 |
| 11. | 0.60 | 0.60 | 1.1 | 11. | 0.18 | 0.56 | 0.1 | 11. | 0.19 | 0.47 | 0.1 |
| 12. | 0.32 | 0.46 | 1.1 | 12. | 0.27 | 0.51 | 0.8 | 12. | 0.46 | 0.59 | 0.5 |
| 13. | 0.21 | 0.32 | 0.9 | 13. | 0.34 | 0.42 | 0.5 | 13. | 0.19 | 0.41 | 0.1 |
| 14. | 0.28 | 0.37 | 0.7 | 14. | 0.24 | 0.42 | 1.2 | 14. | 0.30 | 0.36 | 0.8 |
| 15. | 0.30 | 0.46 | 0.7 | | | | | | | | |
| 16. | 0.18 | 0.46 | 0.4 | | | | | | | | |
| 17. | 0.53 | 0.57 | 1.4 | | | | | | | | |
| 18. | 0.33 | 0.44 | 2.2 | | | | | | | | |
| 19. | 0.29 | 0.38 | 1.2 | | | | | | | | |
| 20. | 0.16 | 0.16 | 1.3 | | | | | | | | |

## Beach
All samples from high-tide line

|  | MdP | MdQ | Per cent P |
|---|---|---|---|
| Tybee Island, middle | 0.15 | 0.17 | 1.9 |
| Ossabaw Island, North end | 0.15 | 0.17 | 0.9 |
| St. Catherines Island, middle | 0.18 | 0.33 | 2.9 |
| Sapelo Island, North end | 0.17 | 0.17 | 4.1 |
| Sapelo Island, middle | 0.11 | 0.17 | 1.1 |
| Sea Island, South end | 0.10 | 0.17 | 0.8 |
| Jekyll Island, North end | 0.14 | 0.20 | 0.3 |
| Cumberland Island, North end | 0.16 | 0.18 | 0.3 |
| Fernandina Island, North end | 0.16 | 0.18 | 0.5 |

## Estuaries (Sounds)

|  | MdP | MdQ | Per cent P |
|---|---|---|---|
| St. Catherines Sound, inner | 0.09 | 0.15 | 1.7 |
| St. Catherines Sound, middle | 0.19 | 0.39 | 0.3 |
| St. Catherines Sound, mouth | 0.56 | 0.46 | 0.3 |
| Sapelo Sound, inner | 0.17 | 0.36 | 0.2 |
| Sapelo Sound, mouth | 0.08 | 0.20 | 0.1 |
| Doboy Sound, inner | 0.37 | 0.36 | 2.8 |
| Doboy Sound, mouth | 0.15 | 0.18 | 1.3 |
| Altamaha Sound, middle | 0.09 | 0.24 | 0.5 |
| Altamaha Sound, middle | 0.17 | 0.75 | 0.1 |
| Altamaha Sound, mouth | 0.17 | 0.41 | 0.1 |
| Altamaha Sound, mouth | 0.14 | 0.17 | 4.9 |

## SHALLOW WATER PHOSPHORITES

*Sir:* In his recent paper (25) and more recent discussion (26) of my paper (31) McConnell has clearly concluded that most phosphorites (marine strata consisting predominantly of carbonate apatite) have originated by direct precipitation under "biochemical influence" in a manner analogous to the formation of teeth and bone. McConnell implies that phosphorite is precipitated directly from sea water with the possible aid of the enzyme carbonic anhydrase and maintains that ". . . the necessary conditions for precipitation probably cannot be evaluated solely by means of inorganic chemical theory" (25). McConnell agrees that some phosphorites do form by alteration of limestone or other materials, but goes on to state that the application of this concept to ". . . many, if not most phosphorites" is an ". . . unjustifiable simplification of geologic processes . . ." (25).

It is my contention, in view of the present state of our knowledge, that replacement of calcarious sediments is the only reasonable mechanism of phosphorite formation. Any theory of phosphorite formation must account for several well established geologic facts: 1) deposition in shallow water (6, 32) : 2) formation of deposits during nearly every geologic period since the Cambrian (24, 36) ; and 3) common association of phosphorite with calcareous sediments (14, 18, 23, 32). Two geochemical factors must also be considered : 1) a mechanism of precipitation, and 2) a local concentration of phosphate sufficient to cause precipitation by the mechanism proposed. Several of the modes of formation that have been proposed by various authors will be criticised below with respect to geochemical considerations.

Direct inorganic precipitation from sea water saturated with respect to phosphorite is the mechanism proposed by Kasakov (20), Dietz *et al.* (12), McKelvey (29), Sheldon (37), and others. Local rise in pH or temperature brings about supersaturation and precipitation. These writers have proposed marine upwellings as the source of phosphorous-rich waters, but biologically productive near-shore environments, especially estuaries, can maintain high phosphate values independently of upwelling and thus offer an alternate source (6, 11, 31, 45). As supporting evidence Dietz *et al.* have calculated that Pacific Ocean waters are supersaturated with respect to $Ca_3(PO_4)_2$. Subsequently (1) marine phosphorite has been shown to be carbonate fluorapatite : $Ca_5(PO_4, CO_3, OH)_3F$ indicating Dietz's results can no longer be considered realistic.

As a word of caution: it is highly improbable that all the phosphorous in sea water is present as simple biphosphate and phosphate ions. Kramer (22) has mentioned the complex ions $Ca_2HPO_4CO_3^0$ and $Ca_2PO_4CO_3^-$ and it is also possible that much "inorganic phosphate" reported in sea water is in reality complexed with organic substances. These facts tend to limit the validity of chemical calculations based on reported concentration data.

Recently Kramer (22) has calculated that Pacific Ocean water is supersaturated with respect to carbonate apatite. This is contradicted by the results of Arrhenius (4) who finds that apatite is presently dissolving on the Pacific sea floor. Kramer admits that "some of the assumptions made in doing the calculations may not be valid." Kramer states further that Pacific waters are much more supersaturated with fluorapatite, $Ca_{10}(PO_4)_6F_2$, than with carbonate apatite, yet the latter is always found in sediments rather than the former, suggesting that factors other than solubility relations control the formation of marine phosphorites. This idea is greatly strengthened by the experimental studies of Klement (21), Arnold (3) and Ames (2) who conclude that carbonate apatite cannot be formed by direct inorganic precipitation from solution.

The last statement needs clarification. Carbonate apatites will be considered to be apatites that contain a few percent carbonate ions substituting for phosphate ions in the apatite lattice (16). Marine phosphorites are predominantly composed of this material (1). As will be discussed later, carbonate apatites can apparently be prepared in the laboratory by a replacement reaction of solid $CaCO_3$ with phosphate ions in solution (2, 38). On the other hand, apatites precipitated directly from aqueous solution (at room temperature) may well contain $CaCO_3$ only as an amorphous or adsorbed phase rather than as an integral part of the crystal structure (21, 2, 3, 42, 41).

McConnell (28) feels that apatites with up to 20 percent carbonate can be precipitated from solution at essentially room temperature and that all the carbonate is present structurally in the apatite (he denies the existence of an adsorbed or amorphous phase). It is impossible to detect the presence or amount of structural carbonate by X-ray powder diffraction or optical data (27, 39). The usual procedure is to measure the Ca/P ratio and if this exceeds 1.67 (the theoretical value for a stoichiometric apatite) then it is assumed that the phosphate deficiency is due to substitution of carbonate for phosphate. However, excess calcium could also result from $CaCO_3$ adsorbed on the fine apatite crystallites or present as a separate phase. McConnell (28) can detect, by X-ray diffraction, carbonate in amounts as small as 2 percent if present as calcite, and claims that some, if not all, precipitated apatites with carbonate in the analysis or with Ca/P greater than 1.67 contain no separate $CaCO_3$ phase. He has also examined such precipitates by optical microscopy and found no separate carbonate phase.

Trautz (42), on the other hand, has pointed out that if the carbonate phase is poorly crystallized or amorphous, then it can be present in amounts up to 20 percent and yet defy identification. Furthermore, Trautz has prepared precipitates from solutions containing carbonate and phosphate ions which are very poorly crystallized or even completely amorphous. It would thus seem reasonable that most laboratory precipitates containing excess calcium and carbonate ions may have a nearly amorphous $CaCO_3$ present as an additional phase.

Lastly, the work of Termine and Posner (40, 41), based in part on infrared studies, shows that carbonate apatites formed by replacement are fundamentally different from those which are directly precipitated from solution. These authors believe that precipitated carbonate apatites contain adsorbed rather than structurally bound carbonate. According to Termine and Posner (41) : "It is probable, then, that [apatites formed by replacement are] far removed, both chemically and structurally from [apatites formed by direct precipitation from aqueous solution] and from bone apatite."

Extrapolating these results to the marine environment, we must conclude that there is some doubt that phosphorites can be direct inorganic precipitates from sea water super-saturated with respect to carbonate apatite. Certainly the rate of formation of some marine phosphorites may be quite slow (12), and under such conditions it is possible that carbonate might be incorporated into the structure. Crystallochemical arguments can also be made that under such circumstances the carbonate, which may tend to make the structure unstable (42), would be completely excluded. In the light of available evidence it would seem that direct inorganic precipitation is no longer a tenable hypothesis for formation of the well crystallized carbonate apatite which constitutes marine phosphorites.

McConnell (25), Cayeux (7), Riggs (32), and perhaps Bushinsky (6) hint that some organic process or organism provides the mechanism of phosphorite production. Both McConnell with his biochemical precipitation and Riggs (32), who proposes that phosphorite is deposited by organisms in areas of upwelling waters, require an abnormally high local concentration of phosphorous in sea water. However, this may not be necessary. Many organisms are able to concentrate elements that are present in very low concentrations in sea water (i.e., certain echinoderms concentrate copper). Thus it might be possible to form a phosphorite deposit by continuous extraction of phosphate from circulating normal sea water. Bushinsky agrees with Pevear (31), Degens (11), and Youssef (45) that organisms can raise the concentration of dissolved phosphate in the sea near productive areas, but does not specify an explicit mechanism for phosphorite formation.

Cayeux (7) and Riggs (33) find what they interpret as fossil bacteria in some phosphorites. Cayeux suggests that these organisms have played an active role in the formation of the phosphorite. McConnell (25) has called attention to the association of bacteria with the formation of mineralized dental calculus (13, 35), which is essentially an apatite. There is some question whether bacteria participate directly in the formation of apatitic material or are only incidentally associated. The authors cited above believe that the bacteria may play an active role. Ennever (13) grew mineralized oral bacteria cultures in "calcifying solutions" not unlike sea water (or saliva) except that they contained more than 100 times as much phosphorous as is found even in high-phosphate sea water. Extracts from bacteria also seemed to initiate apatite-like precipitates. Rizzo et al. (35) grew mineralized oral

bacteria cultures in dialysis tubes implanted within the intestinal cavity of rats. Dead bacteria seemed more susceptable to mineralization than living species.

The fact is that dental calculus (deposits on the teeth) is a complex mass of living and dead bacteria with included food debris, saliva, enzymes, epithelial cells, and so forth. Within such a mass (or within masses of dead cells in vitro) solutions become trapped and phosphate concentration resulting from decay and break-down of organic materials can probably reach high enough values to bring about precipitation of a poorly crystallized hydroxyapatite. The extrapolation of this information to marine conditions is difficult if not impossible. There can be little doubt that microorganisms may be very influential in controlling the character of marine sediments, especially in near-shore areas where nutrients are abundant (30). However, we must, as geologists, heed the advice of Wood (44) : "The relationship between microorganisms and geological processes has been the subject of some wishful thinking, in that geologists have tended to assign to biological agents many things which they could not readily explain. . . ." Although calcium carbonate precipitating marine bacteria have been described (15), none are presently known that will precipitate apatite from sea water.

Vertebrate bones and the shell of *Lingula* are carbonate apatite, as McConnell has pointed out (25). McConnell has also shown that the enzyme carbonic anhydrase may be related to the formation of bone and dental calculus, but the absence of this enzyme from sea water makes unclear how this substance is related to the formation of marine phosphorite. We must conclude, then, that although organisms can raise the dissolved inorganic phosphate concentration of sea water to unusually high levels in near-shore areas of high productivity, they most certainly do not provide any known mechanism for removing this phosphate from the sea (unless all phosphates are accumulation of bone!).

It has long been known that calcium carbonate can be converted to apatite by reaction with dilute solutions of phosphate ions (34). Ames (2) has established that apatites formed in this way contain structural carbonate and are thus carbonate-apatites. So replacement becomes a third mechanism of phosphorite formation. Ames' experiments, using radioisotopes to tag certain ionic species, have nicely illustrated the replacement mechanisms involved. Ames finds that solutions with 0.1 ppm phosphate or greater are required for the replacement reaction to proceed. Pevear (31) has compared Ames' minimum value to actual reported concentrations of phosphate in marine environments and found concentrations high enough to cause phosphatization only in environments such as estuaries, fjords, and upwellings. Youssef's recent work (45) and Bushinsky's early paper (5) suggest replacement as a very likely mechanism for the formation of economic phosphorite deposits.

Degens (11) provides an excellent summary of the phosphorite problem from a geochemical point of view and concludes that replacement of calcium carbonate is the method of formation. Charles (9) comes to similar conclusions. Numerous well-documented examples of phosphatization of calcium carbonate are reported in the literature. Hamilton (17) has described a phosphatized globigerina ooze from the top of a Pacific guyot. Clarke (10) and also Hutchinson (19) note that limestone beds underlying guano deposits are phosphatized by downward moving solutions. Wilcox (43) and Cayeux (8) describe phosphatization of fossils in English and French deposits, respectively. Malde (23) has shown that South Carolina deposits are derived from a phosphatized marl bed. Dietz *et al.* (12), found phosphatized forams on the sea floor off California. Riggs (32) has described replacement of dolomite rhombs in deposits of central Florida. Undoubtedly the list could be made much longer.

Direct inorganic precipitation of carbonate apatite from sea water is probably not possible and no organic or biologic mechanism is presently known to be operative in the marine environment. The replacement process has been observed both in the laboratory and in the field. In the light of the existing data, it appears that inorganic replacement of calcium carbonate by phosphate ions in sea water is the only reasonable mechanism for phosphorite formation.

DAVID R. PEVEAR

UNIVERSITY OF MONTANA,
MISSOULA, MONTANA,
*February 22, 1967*

## REFERENCES

1. Altschuler, Z. S., Cisney, E. A., and Barlow, I. H., 1953, X-ray evidence of the nature of carbonate apatite: Internat. Geol. Cong., 19th, Algiers, 1952, Comptes rendus, Sec. II, pt. II, p. 9 (abstract).
2. Ames, L. L., Jr., 1959, The genesis of Carbonate apatites: ECON. GEOL., v. 54, p. 829–841.
3. Arnold, P. W., 1950, The nature of precipitated calcium phosphates: Faraday Soc. Trans., v. 46, p. 1061–1072.
4. Arrhenius, G., 1963, Pelagic Sedimentation. In: M. N. Hill (ed.), The Sea, v. 3, Interscience, New York, p. 655–727.
5. Bushinsky, G. I., 1935, Structure and origin of phosphorites of the U.S.S.R.: Jour. Sed. Pet., v. 5, p. 81–92.
6. ——, 1964, On shallow water origin of phosphorite sediments. In: L. M. J. U. Van Straaten (ed.), Developments in Sedimentology, v. 1, Elsevier, Amsterdam, p. 62–70.
7. Cayeux, L., 1936, Existence de nombreuses bacteries dans les phosphates sedimentaries de tout age: C. R. Ac. Sci., t. 203, p. 1198–1200.
8. ——, 1939, Les Phosphates de Chaux Sedimentaires: Etudes des Gites Mineraux de la France (serv. cart. Geol. Fr.) tome 1, national press, Paris.
9. Charles, Georges, 1953, Sur l'origine des gisements de phosphates de chaux sedimentaries: Internat. Geol. Cong., 19th, Algiers, 1952, Comptes rendus, sec. II, pt. II, p. 163–184.
10. Clarke, F. W., 1924, The Data of Geochemistry: U. S. Geol. Survey, Bull. 770.
11. Degens, E. T., 1965, Geochemistry of Sediments: New Jersey, Prentice-Hall, 342 p.
12. Dietz, R. S., Emery, K. O., and Shepard, F. P., 1942, Phosphorite deposits on the sea floor off southern California: Geol. Soc. America Bull., v. 53, p. 815–843.
13. Ennever, J., 1963, Microbiologic calcification: Ann. New York Acad. Sci., v. 109, p. 4–13.
14. Grabau, A. W., 1919, Prevailing stratigraphic relationships of the bedded phosphate deposits of Europe, N. Africa, and N. America: Abstract, Geol. Soc. America Bull., v. 30, p. 104.

15. Greenfield, Leonard, 1963, Metabolism and concentration of Ca and Mg and precipitation of CaCO₃ by a marine bacterium: Ann. New York Acad. Sci., v. 109, p. 23–45.
16. Gruner, J. W., and McConnell, D., 1937, The problem of the carbonate apatites, The structure of francolite: Z. Kristallog., v. 97A, p. 208–215.
17. Hamilton, E. L., 1956, Sunken islands of the mid-Pacific mountains: Geol. Soc. America Memoir 64, 97 p.
18. Hendricks, S. B., Hill, W. L., Jacob, K. D., and Jefferson, M. E., 1931, Structural characteristics of apatite-like substances and composition of phosphate rock and bone as determined from microscopial and X-ray diffraction examinations: Ind. and Eng. Chemistry, v. 23, p. 1413–1418.
19. Hutchinson, G. E., 1950, The biogeochemistry of vertebrate excretion: Am. Mus. Nat. Hist. Bull., v. 96, 544 p.
20. Kasakov, A. V., 1937, The phosphorite facies and the genesis of phosphorites. In: geological investigations of agricultural ores: Leningrad Sci. Inst. Fertilizers and insecto-fungacides trans. (U.S.S.R.), no. 142, p. 95–113.
21. Klement, R., Huter, F., and Kohrer, K., 1942, Bildet sich carbonate apatit in wasserigen systemem: Zeitschr. Electrochemie, Band 48, mr. 6, p. 334–336.
22. Kramer, J. R., 1964, Sea water: saturation with apatites and carbonates: Science, v. 146, p. 637–638.
23. Malde, H. E., 1959, Geology of the Charleston phosphate area, South Carolina: U. S. Geol. Survey Bull. 1079, 105 p.
24. Mansfield, G. R., 1940, Phosphate deposits of the United States: Econ. Geol., v. 35, p. 405–429.
25. McConnell, D., 1965, Precipitation of phosphates in sea water: Econ. Geol., v. 60, p. 1059–1062.
26. ——, 1966, Shallow-water phosphorites: Econ. Geol., v. 61, p. 967–968.
27. ——, 1965, Crystal chemistry of hydroxyapatite, its relation to bone mineral: Arch. oral Biol., v. 10, p. 421–431.
28. ——, 1966, Written communication.
29. McKelvey, V. E., Swanson, R. W., and Richards, R. P., 1953, The Permian phosphorite deposits of western United States: Internat. Geol. Cong., 19th, Algiers, 1952, Comptes rendus, sec. II, pt. II, p. 45–64.
30. Oppenheimer, Carl H., 1960, Bacterial activity in sediments of shallow marine bays: Geochem. et Cosmochim. Acta, v. 19, p. 244–260.
31. Pevear, D. R., The estuarine formation of United States Atlantic Coastal Plain phosphorite: Econ. Geol., v. 61, p. 251–256.
32. Riggs, S. R., and Freas, D. H., 1965, Stratigraphy and sedimentation of phosphorite in the central Florida phosphate district: A.I.M.E. preprint no. 65H84, 17 p.
33. ——, 1966, Personal communication.
34. Riviere, A., 1941, Recherches experimentales sur la sedimentation phosphatee en milieu marin: Acad. Sci. Paris, Comptes rendus, v. 212, p. 1038–1041.
35. Rizzo, A. A., Scott, D. B., and Bladen, H. A., 1963, Calcification of oral bacteria: Ann. New York Acad. Sci., v. 109, p. 14–22.
36. Ronov, A. V., and Korzina, G. A., 1961, Phosphorus in sedimentary rocks: Geokhimiya, in translation, 1960, no. 8, p. 805–829.
37. Sheldon, R. P., 1964, Exploration for phosphorite in Turkey—a case history: Econ. Geol., v. 59, p. 1159–1175.
38. Simpson, Dale R., 1964, The nature of alkali carbonate apatites: Am. Mineralogist, v. 49, p. 363–376.
39. ——, 1965, Carbonate in hydroxylapatite: Science, v. 147, p. 501–502.
40. Termine, J. D., and Posner, A. S., 1966, Infrared analysis of rat bone: Age dependency of amorphous and crystalline mineral fractions: Science, v. 153, p. 1523–1525.
41. ——, 1967, infrared absorption of carbonate apatite: discussion: Science, v. 155, p. 607–608.
42. Trautz, Otto R., 1955, X-ray diffraction of biological and synthetic apatites: Ann. New York Acad. Sci., v. 60, p. 696–711.
43. Wilcox, N. R., 1953, The origin of beds of phosphatic chalk with special reference to those at Taplow, England: Internat. Geol. Cong., 19th, Algiers, 1952, Comptes rendus, sec. II., pt. II, p. 120–133.
44. Wood, E. J. F., 1958, The significance of marine microbiology: Bact. Review, v. 22, p. 1–19.
45. Youssef, M. I., 1965, Genesis of bedded phosphates: Econ. Geol., v. 60, p. 590–600.

DISCUSSIONS
DISCUSSIONS
DISCUSSIONS
DISCUSSIONS
DISCUSSIONS
DISCUSSIONS