ORIGIN OF MARINE PHOSPHORITES OFF BAJA CALIFORNIA, MEXICO

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SUMMARY

A bedded phosphorite facies, found within recent continental shelf sediments off the west coast of Baja California (Mexico), between 24° and 26° N latitude, was investigated. Local conditions appear to conform closely with the environmental prerequisites to large-scale phosphate deposition as inferred from observation on ancient marine phosphorites. The deposit occurs on a shallow platform marginal to a trough restricted by submarine banks. Local seasonal upwelling supplies dissolved phosphate to the shelf at an estimated rate of $70 \times 10^{15}$ tons $P_2O_5$/year and effective biological factors are observed to concentrate and deliver yearly at least $3 \times 10^8$ tons $P_2O_5$ to the bottom sediments.

From extrapolations based on measured apatite concentrations at the sediment surface, the mass of the deposit is estimated at $1.5-3 \times 10^9$ tons $P_2O_5$. At least 0.5–1 million years is required for the deposit to accumulate. Such an interval of time for a deposit accumulating at shallow depth allows for profound mixing during transgressive-regressive cycles. Surface concentrations and size distribution of the phosphorite grains, pellets and bioclastic fragments are found to be related to the detrital part of the sediments and influenced by the same mechanical processes. Recent mineralization, if it occurs, has to be synchronous with reworking and is concealed.

Lithologically, the observed association of the carbonate–fluorapatite with opaline silica and reducing fine muds evokes the well-known chert–carbonaceous shales–phosphorite association of ancient rocks. Evidence of current mineralization is rare; few cases of transitions from calcite and dolomite to carbonate–apatite are observed.

Absolute age determinations were attempted on the lattice-bound carbonate of the carbonate–fluorapatite. The dating of fossil apatitic brachiopod valves shows that this structural carbonate is not subsequently exchanged once the mineral is formed. The observed carbon activities, corresponding to apparent ages between 10,000 and 27,000 years, may indicate that some apatite mineralisation has taken

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place recently. Direct observations on the deposit suggests, however, that it is in part older than any carbon date obtained. The $^{238}\text{U}/^{230}\text{Th}$ ratios measured on two size fractions of the same sample correspond to an age of about $2 \cdot 10^5$ years but the applicability of this dating method to marine apatites is still uncertain.

INTRODUCTION

Marine phosphorites are the end-products of imperfectly known processes which are largely inferred from studies of ancient deposits, while little evidence has been gathered from phosphate deposition in the modern seas. Because of the occurrence of phosphorites on submerged continental platforms exposed to frequent upwelling, a general relationship between this dynamic condition and phosphate deposition has been postulated (KASAKOV, 1937). The situation of phosphatic nodules at the sediment–water interface and their internal structure suggest a formation in situ by precipitation from sea water (DIETZ et al., 1942). However the details of the process remain obscure and, among others, the following problems have yet to be answered. Except close to the surface, the oceans should be about saturated with respect to hydroxiapatite (SILLEN, 1960); thus, factors not yet clearly defined must explain why marine apatite deposition is restricted in space and time. The contemporaneity of deposits now on the sea floor is questionable: for the material found on the California Borderland, a Tertiary mineralisation is suggested by microfossils, but it is difficult to ascertain deposition in the present (EMERY, 1960). Phosphate diagenesis of calcium carbonate has clearly been of importance in the origin of some phosphate rock but is rarely observed in recent carbonates. Finally, phosphate is transferred to the sediments largely through the accumulation of organic residues and knowledge on its regeneration within the sediments is imperfect.

Further, dense concentrations of fine-grained phosphorites which make up large fractions of ancient deposits have not been reported in recent sediments even though detrital phosphatic grains are occasionally found. Thus, what has been described as a “bedded phosphorite” facies in the geological column (McKELVEY et al., 1953) has apparently no equivalent in sediments younger than Middle or Late Tertiary and it has been suggested that special conditions may be required (MANSFIELD, 1940).

Recent sediments in some areas of the shelf and nearshore to the west of the Baja California Peninsula (Mexico) contain phosphatic grains as a major constituent. The deposit is present on part of an extensive shallow platform, between 34°30' and 26° N latitude (Fig.1) and general conditions presumed to be favorable to phosphatic deposition are attained. The area represents the southern extension of the California Borderland, the site of the most extensive occurrence of marine phosphorite in modern seas. The possibility that these fine-grained phosphatic sediments could have formed

Fig.1. Known general extent of fine-grained phosphorite occurrence in sediments along the west coast of Baja California, Mexico.
in situ and be contemporaneous should be examined. Admittedly the deposit is exposed constantly to reworking by marine agents which may rapidly obscure any evidence of a recent local derivation, but even these transformations may be significant as former shallow deposits necessarily went through similar stages.

The project did not include any investigations on the chemistry of deposition but was planned as a regional study aimed at recognizing and describing a possible modern equivalent of a common phosphatic lithofacies. Studies were carried out first to establish the distribution of the phosphorites over the shelf and their relationship to the present sedimentary framework. Also the petrography of the phosphatic grains and any other apatite bearing material was investigated for any element suggestive of recent growth. Thirdly, it was relevant to the problem to examine local conditions which could bring about the deposition of apatite and compare the presently available sources of phosphate to the mass of phosphate estimated for the deposit. Finally an attempt was made to obtain direct evidence on the age of the deposit by radiometric determinations on the apatite itself.

GENERAL CHARACTERISTICS OF THE ENVIRONMENT

Some of the physical conditions prevailing during the early formative stage of ancient bedded phosphorites can be recognized in their lithofacies associations. Most of the deposits occur on or along the flanks of tectonic basins (Eocene from Israel and Egypt, BENTOR, 1953; YOUSSEF, 1965), in conditions of relative isolation from open ocean circulation. Cherts and calcareous black shales rich in organic matter form a typical association with the phosphorites (the "miogeosynclinal facies" of MCKELVEY et al., 1953) also suggesting a partially restricted environment of high productivity. The coast line is not far; fine terrigeneous sediments may be present (Mississippian of Alaska, PATTON and MATZKO, 1959), but the sediment supply should be small to permit high primary grades of phosphate. Associated fossils and abundant criteria of reworking in some occurrences suggest shallow water (Cambrian of Russia, BUSHINSKI, 1964; Upper Jurassic of Mexico, ROGERS et al., 1953). A warm arid climate best suits the low sedimentation and high productivity. Lateral facies changes are often indicative of a pene-contemporaneous marine transgression (Permian deposits of the U.S., MCKELVEY et al., 1953), often resulting in the development of a deposit by reworking of previously formed phosphorites (Jurassic of the Russian platform, KASAKOV, 1937).

In the light of these observations, the Santo Domingo embayment off Baja California could represent a likely zone of phosphatic deposition. The shelf is a shallow platform of little relief, approximately 13,000 km² in surface area and up to 80 km wide (see Fig.1 for location of area). A faulted basin more than three times the average depth of this submerged plain is marginal on the west and is flanked along the continental slope by a line of escarpments 100 km long. These form shallow banks less than 50 m deep (Fig.2). In various places they appear on the echograms
Fig. 2. General bathymetry of the continental shelf and offshore banks in the main area of phosphorite occurrence.

to have been leveled off at approximately 100 m and may have been subaerially exposed during periods of lower sea levels, transforming the present shelf into an embayment similar to Bahia Magdalena to the south. At present these submarine ridges form a sill limiting the free exchange of water between the shelf and the open ocean.

A semi-arid climate characterizes the region. Annual precipitation averages about 12 cm (Aschman, 1959), occurring mostly in the summer and fall. An undu-
lating coastal plain of low relief with isolated mesas extends along the coast, covered only with a desertic vegetation of shrubs. It is dissected by a few streams which remain dry except during rare torrential rainfalls. Their deeply entrenched channels support the evidence of a wetter climate in the recent past (Arnold, 1957). To the south the coastline is fringed for 30 km or more by lagoons covered with an extensive mangrove growth and protected by wide dune-covered barriers. Tides are only 1.5–2 m in range but the associated turbulence at the inlets is sufficient to maintain much fine material in suspension. Longshore currents generated mostly by northwest swells have a net southward flow and feed the lagoon barriers with material originally derived from the stream and cliff area to the center of the embayment.

Geological information on the surface and subsurface rocks along the coast (Mina, 1957), supplemented by data from a sonic profile of the offshore area, suggests that the shelf is an erosional platform cut into the west flank of the Baja California syncline complex. This is a thick series of Tertiary sediments of dominantly marine origin with intercalated volcanics more than 4,000 m thick. A Middle Miocene unconformity is found regionally on rocks similar in lithology to the Monterey Formation of southern California. This unconformity dips from the surface along the northern reach of the coastal plain to 100 m or more below the floor of the lagoon at the southern end. It can be followed offshore as a subbottom reflector on the sonic record. If, as in southern California, a phosphiatic facies is associated with the diatomaceous facies observed in these Miocene rocks, it should be a likely source for detrital phosphorite. No phosphorite, however, has been reported either in the type sections studied (Heim, 1922; Beal, 1948) or the drill logs (Mina, 1957).

The local hydrography is influenced by two large-scale features of the eastern Pacific circulation. Upwelling, a stable seasonal feature resulting from a recurrent pattern of atmospheric conditions along the California coast, has marked intensity in southern Baja California during April, May and June and is particularly intense south of promontories such as Punta Eugenia and Punta Abreojos. Also at the latitude of Santo Domingo a convergence takes place between water of the California Current and north-bound North Equatorial water (Reid et al., 1958). Cold water coming from the north overrides the more saline, oxygen depleted, nutrient-rich waters flowing from the south and a layer of mixed origin is formed at depths of 200 m or more. It maintains regionally an oxygen minimum layer (< 0.2 ml/l O2) and a phosphate maximum layer (> 3.5 μg atm./l PO4-P) which are much closer to the surface than those found in areas of the California current to the north. The edge of the shelf is also at about 200 m and little energy is required to displace waters deficient in oxygen and enriched in nutrients over the banks, into the marginal trough and over the shelf in periods of upwelling. At this time of the year measurements indicated very low values of dissolved oxygen on the shelf and oxygen starvation in the basin (Fig.3). The restricting bottom topography, the oxygen deficiency of the incoming waters and the high zooplankton productivity observed during the spring upwelling concur to favor the deposition and preservation of large volumes of organic detritus in the sediments. The concentration and transfer of phosphate from
Fig. 3. Three northeast, southwest hydrographic sections showing dissolved oxygen (ml per liter) in waters above the outer shelf, the offshore basin and banks at the time of upwelling.

The general oceanic reservoir to the local basin is highly favored by this natural scheme.

COMPOSITION AND PETROGRAPHIC DESCRIPTION OF THE PHOSPHORITES

The phosphorites of Baja California occur as well sorted, sand-sized particles dominantly calcium phosphate in composition, within a fine sand to silt matrix. The calcium phosphate is present as a carbonate-rich member of the apatite series known as carbonate-fluorapatite (ALTSCHULER et al., 1958). In the lattice carbonate

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groups are believed to substitute for PO₄ groups (McConnell, 1952), the electrostatic balance being maintained partly by the substitution of fluorine for oxygen, while coupled substitution of Ca²⁺ and P⁵⁺ by various cations of lesser valence has also been suggested. The composition of the mineral may be described by the following general formula: Ca₁₀(PO₄, CO₃)₆F₂₋₃. The carbonate content may vary according to the extent of the substitution and it is difficult to differentiate analytically between the CO₂ contributed by any associated calcite and that which is intrinsic to the apatite (Lodding, 1964). By the use of differential solvents for calcite, and monometric determinations of the remaining carbonate, the carbonate content of the apatite in the deposits under study was empirically determined to be 1.25 to 1.75 % CO₂ by weight (Table I). Thus it is somewhat lower than the 2.29 % CO₂ found in artificially made carbonate-fluorapatite by Simpson (1965), but compares with the values determined by Silverman et al. (1952) for the Permian type deposits of Wyoming and with those obtained for the large nodules commonly occurring on the borderland of southern California. The fluorine content (2.8 %, average of two determinations) is also similar to that of these two materials.

Carbonate-fluorapatite makes up about 90 % by weight of the phosphate particles, the remainder being composed of detrital inclusions, syngenetic sulfides, organic matter, opaline silica and disseminated calcite. The mean P₂O₅ content from two analyses of the apatite particles is 30.2 %.

Two distinct types of phosphate particles can be recognized:

(1) Black ovoidal structureless pellets are predominant in grain sizes between 0.125 and 0.250 mm.

(2) Particles of biogenous origin are predominant in the coarser fractions. The majority of the biogenous particles are platy and lamellar and appear to be derived from a phosphatic brachiopod valve (Disciniscus cumingii Broderip, 1886). Abrasion has generally not affected the irregular surfaces of the pellets, characterized by knobby protrusions and cavities (Plate IA). In thin sections the pellets are normally structureless, with only occasional apparent concentricity due to zonal staining by diffuse organic matter (Emigh, 1958). A superficial reduction layer imparts a black color to the pellets collected in the reducing zone of the middle continental shelf, but it is absent in the reddish brown pellets from the oxidizing environment of the beach.

Opaline silica is an important constituent of the pellets. It occurs as a whitish filling in surface cavities and as a very fine surface film which may be concentrated.

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**PLATE I**

A. Phosphatic grains from the continental shelf, size fraction 0.125-0.250 mm.
B. Residual envelopes of intermixed apatite and opaline silica obtained after partial leaching of the phosphatic pellets in 1N HCl followed by digestion in H₂O₂ (× 250).
C. Part of a phosphatic pellet in thin section, under cross-nicols (× 1500). Circular arrangement of apatite crystals in a groundmass of optically amorphous apatite with dark organic inclusions (note black honeycomb structure toward lower left).
D. Partly phosphatized foraminifera viewed in thin section (cross-nicols). White areas are calcite; darker areas, mixture of glauconite and apatite (× 500).

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in residual greyish envelopes by controlled acid leaching of the pellets in 1 N HCl (Plate IB). They dissociate upon longer exposure to acid. Under the microscope they appear to be made of an intergrowth of about 10% silica and 90% apatite. Diatom fragments which may supply a source for both the silica and the phosphate are detected as inclusions in the groundmass of some pellets (Plate IC). Similar coatings of silica have been observed in ancient fine-grained phosphorites (O'BRIEN, 1953).

The apatite within the pellets occurs both as anhedral, equant crystals a few microns in dimension and as a cryptocrystalline, optically amorphous groundmass surrounding these crystals. These are often grouped as circular mosaics around black organic inclusions (Plate IC).

Fine detrital particles of quartz and feldspar are scattered randomly within the phosphatic groundmass of the pellets. The feldspars are usually deeply altered. Also, hornblende, magnetite, epidote, hypersthene, zircon, sphene and garnet, a ferromagnesian suite comparable to that found in the enclosing sediments, are recovered after solution of the pellets with hot nitric acid. Two accessories typical of these sediments have not been detected in the apatitic groundmass of the pellets. These are dolomite occurring as rhombs in the silt fraction and a zeolite, heulandite or clinoptilolite, found in the finer fraction (Fig. 4).

A black residue obtained after leaching of the pellets with dilute acetic acid, buffered at pH 4.5, is found to contain pyrite, which from the sulfur content determined chemically is estimated to make up ca. 2% by weight of the original pellets. Fluorite is found associated, either as a naturally occurring accessory or as a reaction product, with the residual silica-rich envelope described above. Clays associated with the apatite in the matrix of the pellets were isolated by treatment of the material in dilute hydrochloric acid (0.05 N). These clays gave sharp 10Å first, second and third basal X-ray (CuKα) reflections, suggesting illite as the dominant mineral. Glauconite is found only rarely in the pellets. In contrast, montmorillonite is the predominant clay in the local sediments (Fig. 3).

Thus apart from the associated silica, these fine-grained phosphorites are

| TABLE I |
| WEIGHT PER CENT CO₂ (CARBONATE) OF DATED SAMPLES AFTER PREPARATION¹ |
| Sample No. (See Table II) | Weight % CO₂ (Carbonate) (means of 3 analyses) |
| 1 | 1.44 |
| 3 | 1.55 |
| 4 | 1.33 |
| 6 (48 hrs in excess CaCO₃ solvent) | 1.74 |
| (96 hrs in excess CaCO₃ solvent) | 1.49 |
| (3 weeks in excess CaCO₃ solvent) | 1.59 |

¹ Monometric determinations
similar in mineralogy, composition and general lack of internal structure of the grains to those of ancient deposits (Visse, 1948; Emigh, 1958; Yousef, 1965).

**SEDIMENT TYPES ON THE CONTINENTAL SHELF AND PHOSPHATIC GRAIN DISTRIBUTION**

Certain lithological associations are commonly found with marine phosphate rocks believed to have formed in situ. Occurrences of bedded phosphorites with cherts, siliceous mudstones, calcareous black shales are typical at all levels of the geological column and thus provide criteria to deduce the most likely environmental conditions (Bentor, 1953; McKelvey et al., 1953; Buchinski, 1964; Yousef, 1965).
These are only approximate, as association in interlayered suites actually reflects an oscillation of conditions and a certain range of incompatibility. However, phosphorites and carbonates are less frequently found together (McKelvey et al., 1953) and intermixing of phosphorites with nearshore sands is normally indicative of a phase of transportation or reworking (Visse, 1948). It is thus essential to consider the sedimentary framework of phosphorites present in a likely basin of accumulation.

Sediment types

A study of grain-size distribution on the Santo Domingo shelf indicates a predominance of fine material. Sediments on the platform having their modal size well into the clay–silt range occur at all depths, including in front of the lagoon inlets at the south east (Fig. 5). Very fine sands (0.062 mm–0.125 mm) occur marginally to the north. A tongue of coarser sediments all having their modes in the fine sand range (0.125 mm–0.250 mm) radiates to depths of about 80 m from the central part of the embayment. When extended beyond the present shore, the five local stream channels converge within this deeper zone. Even in areas of sandy bottom, silts and clays represent an important fraction of the sediments.

On the floor and slopes of the offshore trough the sediments are greenish clay-sized muds, smelling strongly of \( \text{H}_2\text{S} \). All cores collected from these areas show irregular faint to conspicuous dark laminations 1–5 mm thick. They appear to be thin reducing zones, possibly corresponding to maxima in the supply of organic residues during years or seasons of higher productivity.

In between extensive rock outcrops the surface of the longitudinal banks marking the termination of the shelf, as well as that of the upper slopes, are covered with a compact layer of foraminiferal ooze (up to 80 \% \( \text{CaCO}_3 \)). In places glauconite, either the dark or the pale green variety, is abundant as internal molds of foraminiferal tests.

Sediments across the entire shelf are mainly reducing. Redox potential measurements taken on board ship on freshly opened cores indicate at the sediment surface a predominance of negative redox potentials increasing rapidly downward. Readings above –300 mV are obtained 50 cm below the sediment–water interface in the basin. Negative potentials also prevail in bottom waters. The pH of the sediments varies from between 7.2 to 7.6 at the surface to values close to 8.0 beneath it.

Pyrite was identified in the green muds of the basin. It is present in tiny spherules, mostly in the 0.002–0.033 mm size fraction. X-ray diffraction analysis under FeK radiations using an internal standard as reference, suggests a downward increase of this mineral in the basin to concentrations reaching 5–6 \% by weight of the total sediment.

Values of organic carbon for surface sediments on the platform, as determined on carbonate free samples in an induction furnace, are normal for this type of environment (1–3 \% by weight). They vary between 5 and 8 \% in the basin. Below the
Fig. 5. General distribution of sediment types on the shelf of the Santo Domingo region.

sediment surface, similar or higher values are usually found, indicating conditions favorable to the preservation of organic matter.

Distribution of the phosphatic grains

No marked contrasts in physical and chemical environment are detectable over the Santo Domingo shelf as a whole, while small but significant differences in grain
Fig. 6. Phosphate distribution on the continental shelf. Numbers represent weight per cent of fine-grained phosphorite in the surface sediments. Black dots: samples containing phosphorite. Open circles: samples lacking phosphorite.

size and sediment composition are noted. It was found important to investigate to what extent the distribution of the phosphorites correlates with variations in the sediment types, or if it is independent of them and reflects the uniformity of the environment. The distribution of apatite concentrations over the surface of the shelf and at depth in the cores was studied quantitatively by X-ray powder diffraction analysis.
of more than 80 samples. The main peak intensity of apatite was measured by scanning at 0.2° interval using a fixed count technique and compared to a nearby reflection of gibbsite blended into the powdered sample as an internal standard. This method allowed the recognition of 2% by weight apatite in a sample.

The results of this survey indicate a definite correlation between phosphatic concentrations and the coarser sediments (fine sand) observed in the continental platform offshore. The higher values are grouped within a circular area 15–20 miles in diameter, at a depth of 50–100 m (Fig.6). There, the surface phosphate distribution fluctuates over short distances and varies between 15 and 40% by weight of the total sediments. These values are of the same order as those obtained on samples from the barrier and lagoons. Concentrations in the nearshore area appear to be somewhat lower, possibly because of dilution by littoral transport.

Beyond the 100 m contour, apatite concentrations drop quickly to near zero values. Low phosphate concentrations, below 5% apatite by weight, are usually associated with the finer muds in and around the basin, and with the carbonate deposits of the banks and upper slopes. Surface concentrations are persistent vertically to the depth of 4 ft. reached by the cores, with no systematic variations. On the narrow continental shelves, extending north and south of the Santo Domingo platform to Punta Eugenia and Bahia Magdalena respectively, (Fig.1), minor amounts of phosphate occur sporadically. Size fractionation of samples from these marginal areas indicate that apatite is present only in the coarser sizes and has a fragmented detrital appearance. Onshore, phosphate pellets are found in the dunes of the modern barrier. They are also present in ancient dunes half-buried amidst the mangrove swamps of the lagoon, which are indicative of various steps in the progradation of the coastline. Concentrations of apatite between 10 and 20% are common there.

Quantitative analyses were made of apatite in weighed sieved fractions of various samples from onshore and offshore stations. From these one can calculate separate size distributions for the phosphatic and the non-phosphatic components. Comparison of the two related histograms gives an indication of the amount of intermixing between pellets and detrital grains (Fig.7); the modes of the two distributions are usually found to coincide, an indication of similar histories of transportation or reworking. The deviation measure (ϕ), a measure of dispersion or sorting (INMAN, 1952), indicates that both components are well sorted (< 0.5). The phosphatic grains, with a modal specific gravity found to be between 2.7 and 2.8, do not differ markedly in this respect from an average specific gravity for the intermixed detrital grains. The spheroidal shape of the phosphatic particles, however, results in different behaviour under gravity, as was observed in dune faces of the barrier islands and in experiments in the laboratory, and this causes some preferential sorting of the phosphate.

A noticeable feature of the phosphatic grain-size distribution is its discontinuity at both ends, particularly toward the fine sizes. In fractions below 0.062 mm, the apatite content does not exceed one or two per cent by weight of the sediments. This narrow variation in size of the granular phosphorites, with a modal dimension around 0.1 to 0.2 mm, has been observed in many other deposits (Visse, 1948; McKelvey

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Fig. 7. Histograms showing the size distribution of apatite grains with respect to the remaining sediment grains in four samples, two from the shore area, two from offshore stations.
PLATE II

A. Dolomite partly replaced by apatite. Thin section of a phosphatic pebble of nodular shape from the offshore banks. Non-phosphatized dolomite pebbles occur nearby (× 500).

B. Silt grains (0.002mm-0.062mm) encrusted with apatite-bearing material.
et al., 1953). It appears to be an original property of the grain population rather than a result of sorting, as no silt-size apatite grains occur in the silt covered areas of the shelf.

Abundant nodular phosphate pebbles were dredged on the flat surface of the offshore banks at depths of 100–200 m. Thin-section examination indicates that they have resulted from partial to complete replacement of carbonate rock by apatite. Fragments of partly replaced dolomite in which apatite is found developing at the periphery and along cleavage planes of dolomite rhombs occur among unaltered pieces of dolomite (Plate IIA). Large quantities of a phosphatized foraminiferal limestone with a recognizable Miocene species (Siphogerina bremerii BRAGG; N. Allison, personal communication, 1963) were dredged from other stations on the banks. Some phosphate rock debris is identifiable in dredge hauls from along the cliffs of Bahia San Juanico, evidence that phosphorite of this type is in part secondary from eroded Tertiary rocks. This material did not include any pellet aggregates.

An estimate of the mass of phosphate in the fine-grained deposit can be made by assuming an average thickness of 20 m, the average depth of the deepest drill samples known to have been recovered in mining explorations of the deposits a few years ago, over an area of maximum concentration approximately 1,800 km². If the average content in apatite is taken to be 5% by weight of the sediments, a low value, the total mass of fine-grained phosphorite (average specific gravity 2.8) is at least $5 \times 10^{15}$ grams of phosphorite, equivalent to $1.5 \times 10^9$ tons P₂O₅. The highest reasonable values for thickness, area and concentration give as a maximum estimate about $4 \times 10^9$ tons P₂O₅. In reference to the Phosphoria formation, estimated to contain $1.7 \times 10^{12}$ tons P₂O₅ (McKelvey et al., 1953), the present deposit is indeed small.

THE QUESTION OF IN SITU FORMATION OR DETRITAL ORIGIN

It is evident that the phosphorite distribution on the Santo Domingo platform is controlled by the same processes of reworking as the detrital components of the sediments, and the phosphate and nonphosphate fractions are deeply intermixed. The recent deposition of the phosphorites, or alternatively the increment of a deposit inherited from local rock weathering, may be obscured by intense shallow water reworking, specially during the last transgression. Thus the possibility that the deposit occurs near its actual site of formation and that slow mineralisation takes place in the present situation has to be considered.

Present supply of phosphate

A survey of the various forms of phosphate locally available and of the quantities presently diverted to the sediments on the shelf is useful to estimate the minimum time required for the accumulation of adequate phosphate reserves.

During a summer survey, concentrations of PO₄-P around 3.5 µg-atm/l were
found in the bottom waters. Thus even at the outset of upwelling, the dissolved phosphate is not above normal for coastal waters in the Eastern Pacific. The theoretical equilibrium values of dissolved phosphate at saturation of apatite are probably not as great: according to Sillen (1960) sea water at 25°C with a pH of 7.6—an average for bottom waters here—is approximately saturated with hydroxapatite when the PO₄-P concentrations reach 2 µg-atm./l. Thus under normal conditions saturation would be reached at various parts of the water column and factors other than ionic concentrations retard the formation of the mineral.

The average yearly turnover of dissolved phosphate through upwelling on the shelf may be computed assuming that the rate of offshore Ekman transport in the spring at this latitude, 9 kg/cm sec, as calculated by Wooster and Reid (1963), is maintained for 6 months a year along the 225 km shelf. The phosphate concentration of upwelled waters is taken to be on the average 2.5 µg-atm./l PO₄-P, a conservative value since at 300 m along the slope, phosphate concentrations are above 3 µg-atm./l (NORPAC Committee, 1960). This gives an average yearly supply of dissolved phosphate of about 7 • 10¹⁵ tons equivalent P₂O₅. However, this preformed phosphate must be only a moderate fraction of the total mass of phosphate present at any time in the waters: from temperature, oxygen and phosphate data, an oxidative fraction (P_Ox) may be calculated in the manner described by Redfield et al. (1963). Oxidative phosphate should represent around 70 % of the total phosphate, thus indicating the importance of phosphate locally bound in organic matter compared with phosphate brought in from outside of the basin.

Estimates of the mass of phosphate permanently removed to the sediments can be based on general computations on the production of organic matter over the Santo Domingo platform. Studying the organic budget for the whole southern California borderland, Emery (1960) concluded that less than 1% of the organic matter produced was permanently lost. He assumed the production to vary between 500 and 1,000 g C/m²/year. Applying these figures to the 13,000 km² area of the present shelf, the dry weight of organic matter escaping each year to the sediments is about 5 • 10⁴ tons. Dry planktonic matter contains about 1% phosphorus by weight (Sverdrup et al., 1942). Thus at this rate, from 2 to 4 • 10⁸ tons P₂O₅ equivalent are extracted each year from the ocean by the bottom deposits. The higher value is probably closer to the actual facts: local zooplankton standing crops are higher than for most parts of southern California thus suggesting a higher average productivity; shallow depths and very low dissolved oxygen decrease the chances of regeneration of sinking organic matter; because of the negative oxidation potentials observed in the sediments there is probably less than one-third of the organic matter at the bottom being oxidized after burial, as assumed by Emery (1960).

Figures of the same order are obtained by considering the yearly production of benthic invertebrates. An active standing crop of scavengers may be considered to use up a large fraction of the nutrients made available at the bottom by sinking organic matter. The local benthos is dominated by a decapod crab (Pleuroncodes planipes Stimpson) which appears to consume large amounts of phosphate in the

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buildup of its hard parts (2.36% P₂O₅ dry weight), and therefore acts as an important factor in phosphate concentration at the bottom. Its progressive adaptation from a pelagic to a benthic mode of living may also be significant with respect to the migration of phosphate from the surface to the bottom. Its maximum population density occurs between Bahia Vizcaino and the end of Baja California at depths between 75 and 300 m (Boyd, 1960), thus coinciding generally with the zone of highly phosphatic sediments on the shelf. The average standing crop of Pleuroncodes at the bottom is about 10 individuals/m². Assuming steady conditions, the mean quantity of phosphate delivered annually to the top layer of sediments by this organism alone is approximately 3,000 tons P₂O₅. The phosphorus in the carapace of this organism is not present as apatite, but may be associated with the magnesium-rich calcite found in the chitinous cuticle of the crab. Little chitinous debris is found in the sediments and no chitin could be identified by tests run on the organic residues of the phosphorites.

At the present rate of phosphate accumulation, it would therefore require at least one half to one million years to accumulate the minimum mass of about 2 billion tons phosphate (P₂O₅) estimated for the deposits. This is true only if the apatite derives its phosphate from organic sources within the sediments rather than from phosphate dissolved in the overlying waters.

**Mineralogical evidence of recent apatite**

The proportion of the major elements in the apatite is similar to large in situ marine nodules found off California and also to old phosphorites of the Permian Phosphoria Formation. Trace elements, at the level of semi-quantitative analysis, are not systematically different from those of other apatites. X-ray diffraction patterns of the few phosphorite grains in the finest (0.043–0.062 mm) fractions of the sediments, assuming that these grains represent incipient deposition, have been compared to those obtained on powdered apatite from the centre of large nodules. There is no definite contrast in the heigh–width ratio of the main apatite peaks to suggest differences in ordering or sizes of crystallites.

Partly phosphatized Recent foraminifera have been collected from the upper continental slope at a depth of 750 m. This case is unique and may have little significance with regard to the origin of the deposit. One core at this station indicated systematic variations in calcium carbonate and calcium phosphate along its length, with apatite increasing from 5% at the surface to 12% at 60 cm while CaCO₃ decreased significantly. The possibility of apatite forming in situ by replacement of biogenous

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**PLATE II**

Photomicrographs of foraminifera with their calcite tests partly replaced by apatite. The tests take on a brownish aspect following replacement. In some cases, pellets made up of apatite and glauconite have developed. 1, 2, 3, 4, 5, 6 = Uvigerina sp.; 7 = Bolivina spissa Cushman; 8 = Cassidulina sp.; 9 = Globigerina sp.; 10 = Planulina sp.; 11 = Globigerinoides sacculifer (Brady) (× 300).

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carbonate is also supported by the microscopic examination of the foraminiferal tests. Thin sections indicate that apatite has substituted for calcite in tests of foraminifera and also that phosphate mineralisation has taken place within the mud-carbonate matrix which filled up the dead organisms (Plate ID). Glauconite pellets also present as internal molds of foraminifera have associated apatite; its diffraction pattern is clearly visible on X-ray diffraction diagrams of carefully separated glauconite grains. X-ray analyses on hand-picked foraminifera which bear signs of replacement also indicate that calcite and apatite are simultaneously present, the replacement being incomplete. The species represented (identification by Mrs. J. Hosmer) are presently living at the approximate depth at which the core was collected. The following ones were identified:

Benthonic species: *Uvigerina* sp.

*Boivina spissa* CUSHMAN

*Planulina* sp.

Planktonic species: *Globigerinoides ruber* (D'ORBIGNY) (probable)

*Globigerina eggeri* RHUMBLER

*Globigerina pachyderma* (EHRENBerg) (probable)

*Uvigerina* sp. is the most abundant species (Plate III).

The importance of this type of replacement in the production of the phosphorite pellets is difficult to evaluate, but the process does not seem to take place on a large enough scale to account for the contemporaneous formation of a large deposit.

Among phosphate pebbles, concretionary in appearance, dredged on the banks a gradation exists between unaltered dolomite fragments, mixed apatite-dolomite types and apatite “nodules” (Plate IIA). This is suggestive of replacement now taking place. The nodular aspect seems to result more from surface rearrangement following substitution of apatite for dolomite than from surface precipitation and accretion. Such substitution was confined to carbonate rock fragments and to the carbonate cement for siltstone fragments. Non-carbonate pebbles, such as phyllite schist or basalt debris also found on the banks, even when deeply altered, had no associated apatite, although phosphate is shown by chemical tests to be present in their limonitic surface, possibly as ferrous phosphate.

Apatite is also found encrusting the surface of the silt-size particles (0.062–0.043 mm) isolated from sediments of the phosphorite-rich zone (Plate IIB). This surface coating flakes off easily and such grains could not be abraded fragments of pellets. Apatite is identified by chemical tests, acid solubility, birefringence and index of refraction. It may represent unique cases of calcium phosphate redeposition around nuclei in the saturated interstitial environment of the deposit, as nothing similar is observed in sediments lying outside the phosphorite-rich zone.

The evidence on present phosphate mineralisation is scanty but sufficient to show that apatite deposition is now taking place by adsorption on and substitution of a carbonate matrix. It supports experimental data on the importance of solid calcium carbonate in initiating apatite deposition (AMES, 1959).
Age criteria from fossil evidence and radiometric measurements

Paleontological evidence on the age of the deposit is scarce. Possibly significant is the finding, at a depth of about 80 m and in a zone rich in phosphorites, of abundant well-preserved valves of a phosphatic brachiopod *Disciniscus cumingii* Broderip 1883 (identified by Dr. N. Allison), known to be Pliocene to Recent in age (Thomson, 1927). This species, reportedly still living along the coast of Central America, is extinct at the latitude of Baja California. Many phosphatic grains of biogenous origin found in the deposits are believed to be fragments of this shell because of easily recognizable laminar structures. Dating by $^{14}$C on the apatite-bound carbonate of the brachiopod shell (see below) indicated an age greater than 50,000 years. The fossil is found embedded within fragments of a limy siltstone in which occasional pellets such as those making up the deposit also occur. This find then suggests that a source of phosphorite may have existed in the now largely vanished local horizons of Pliocene or younger age. Association of pellets and biogenous apatite in the form of brachiopod remains is frequent in ancient deposits.

Definite proof of the contemporaneity of deposition should be provided by any remaining activity from short-lived radioactive isotopes structurally bound to the apatite. The carbonate group is believed to be a structural constituent within the lattice of carbonate-fluorapatite (McConnell, 1952). It is presumably derived from sea water and hence should contribute to the mineral at its formative stage a carbon activity related to that of the water mass from which apatite derived its chemical constituents. The $^{14}$C activity of the apatite may therefore be an index of time of deposition provided the following conditions are fulfilled:

(a) The structurally bound carbon is not exchanged with carbon of the environment during the lifetime of the mineral.

(b) Any adsorbed $^{14}$CO$_2$ is removable.

(c) Calcium carbonate interstitially mixed with the apatite within the phosphorite groundmass, either residual or precipitated after the apatite, can be removed.

(d) In a bulk sample of phosphorite it must be feasible to eliminate any shell fragments present without seriously affecting the phosphorite. Also, the fraction of biogenous phosphatic grains should be small since they are derived from a fossil brachiopod and thus would tend to reduce the activity of the sample.

Since the carbon content of carbonate-fluorapatite does not exceed 1% by weight, about 500 g of phosphatic grains must be separated. This was done in two steps: (1) because of the small range in size of the phosphatic grains, an enriched sample could be obtained by sieving. This step also allowed the elimination of a large fraction of the biogenous apatite which is more frequent above 0.250 mm; (2) the sample was then treated to remove any remaining calcium carbonate. This was done by differential leaching in triammonium citrate (Silverman et al., 1952) or in dilute acetic acid (0.5%). Manometric determinations of carbonate as carbon dioxide in hand-picked phosphatic grains before treatment showed an average value of 5% by weight. After treatment with one of the two solvents, it dropped to between 1 and

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<table>
<thead>
<tr>
<th>Sample</th>
<th>Mes. Ref.</th>
<th>Location</th>
<th>Separation technique</th>
<th>CaCO₃ solvent used</th>
<th>Apatite solvent used</th>
<th>Weight of sample</th>
<th>Date obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LJ-268</td>
<td>dunes on lagoon barrier--Baja California, Mexico (25° 31' N, 112° 08' W)</td>
<td>bromoform</td>
<td>0.05 N acetic acid 48 h with agitation. Sample not ground</td>
<td>—</td>
<td>350 g approx.</td>
<td>19,300 ± 600 years</td>
</tr>
<tr>
<td>2</td>
<td>LJ-399</td>
<td>continental shelf off Baja California Mexico: depth 78.6 m (26° 09' N, 117° 51' W)</td>
<td>CdI₂, KI heavy liquid</td>
<td>Triammonium citrate—48–92 h with agitation. Sample crushed</td>
<td>—</td>
<td>500 g approx.</td>
<td>9,860 ± 200 years</td>
</tr>
<tr>
<td>3</td>
<td>LJ-500</td>
<td>continental shelf off Baja California Mexico: depth 91 m 46 km offshore (25° 45' N, 112° 34' W)</td>
<td>mechanical concentration by sieving of fraction 125–250 µ and repeated washing to remove shell fragments.</td>
<td>0.05 N acetic acid 48 h with agitation. Sample not ground</td>
<td>—</td>
<td>800 g approx.</td>
<td>17,600 ± 450 years</td>
</tr>
<tr>
<td>4</td>
<td>LJ-509</td>
<td>same sample</td>
<td>same</td>
<td>same</td>
<td>1N HCl until 34% of original weight removed</td>
<td>852 g</td>
<td>19,440 ± 600 years</td>
</tr>
<tr>
<td>5</td>
<td>LJ-515</td>
<td>same sample</td>
<td>same</td>
<td>same</td>
<td>1N HCl until 62% of original weight removed</td>
<td>459 g</td>
<td>26,640 ± 600 years</td>
</tr>
<tr>
<td>6</td>
<td>LJ-779</td>
<td>Ground carbonate apatite brachiopod shell (<em>Discinicus cuminii</em> Broderip, 1883)</td>
<td>hand separation of shells. Cleaned with 1N HCl then ground</td>
<td>0.05 N CH₃COOH</td>
<td>—</td>
<td>250 g</td>
<td>— ± 50,000 years</td>
</tr>
</tbody>
</table>

2%, a value which was found to be constant whether the phosphatic grains were treated for 48 h or 3 weeks. The carbonate content was also found to be the same for phosphatic grains, half the mass of which had been removed by HCl (Table I). Furthermore, solution experiments performed on prepared sand-sized mixtures of carbonate shell and phosphate nodule fragments indicated that after one or two days the calcite fragments had gone entirely into solution, while the phosphorite had been only slightly affected. Thus 2 days of treatment appear sufficient to cleanse the samples of all accessible calcium carbonate.

Age determinations were performed by G.S. Bien at the ¹⁴C laboratory of the Scripps Institution of Oceanography, the CO₂ extractions being done by acid hydrolysis in HCl (Hubbs et al., 1962; 1963; 1965). Exact sample locations are listed together with other relevant data and results in Table II.

Sample No. 1 from the lagoon was dated at 19,300 ± 600 years while sample No.2 from the continental shelf gave an age of 9,860 ± 200 years. The difference was apparently reasonable and pointed to the possibility that the phosphorite was deposited offshore.

An experiment was designed to test the validity of these results. It has been thought that phosphorite nodules are concretionary and develop through surface accretion from phosphate colloids in a saturated environment (Dietz et al., 1942). This may be a slow continuous process occurring randomly at the periphery of the nodule and no visible concentricity necessarily ensues. Assuming that pellets are generally formed by this mechanism, progressively older radiocarbon ages should be obtained by removing more and more of the outer material and dating what is left. If increasing ages are obtained and if it can be demonstrated that the pellets are dissolved by HCl from their surface inward, an argument in favor of their origin by accretion would exist.

Samples No.3, 4 and 5 were prepared to test this assumption. Three fractions of phosphorite were obtained from the same large sediment sample collected on the continental shelf at a depth of 90 m. After preliminary treatment to remove the associated calcite, one was dated as such; the two others were leached in HCl (1N) until 36% and 64%, respectively, were removed from their original weights, and the residual material was dated. A series of three increasing ages between 17,000 and 27,000 years was obtained (Table II). However because of the presence of opaline silica film on the surface of the pellets, the HCl solvent attacked them randomly and the end-products were envelopes of silica partially filled with residual masses of apatite. Whether or not the acid removal of the apatite under the outer silica film was generally directional or not was not clear. Thus because of a lack of satisfactory visual control, the evidence gathered by the increasing order of dates remains ambiguous. Minor amounts of recent calcite impurities not removed by the solvent, either in the pellets or as associated fragments, could explain these three dates if during the leaching process this calcite was removed preferentially to the apatite in samples No.4 and 5. In the three samples, no calcite could be detected by any means available. However, because of a much larger carbon content in calcite than in apatite, modern
calcium carbonate in a mixture with apatite having no carbon activity left needs to be only 1% or less by weight to yield the dates obtained.

The possibility of exchange of the structural carbonate was ruled out by dating the fossil brachiopod *Disciniscus cumingii* BRODERIP. Valves and valve fragments of this organism after cleaning according to the above procedure yielded an age greater than 50,000 years. Thus the first condition above and also most probably the last one appear to be satisfied.

Attempts were made to confirm the $^{14}$C ages by the uranium–ionium method (TATSUMOTO and GOLDBERG, 1959), assuming that all the uranium is in the structure of the apatite as $^{U^{4+}}$, according to the evidence put forward by ALTSCHULER et al. (1958) and that the thorium is not initially present or subsequently added to the mineral. The various analyses were performed by M. Koide. Two fractions of the same sample of phosphate pellets showed similar ionium activities corresponding to a concentration in $^{230}$Th of 71 p.p.m. and the age derived for the apatite came to $2.3 \cdot 10^5$ years, after correction for an initial excess $^{234}$U activity of 0.15 (BROECKER, 1963). However, the first of the above assumptions may not be correct: chemisorbed uranyl ions are also present in phosphorites and the proportion of uranium in each valence state was not obtained for the present material. The second condition also may not be satisfied. Furthermore the presence of tetravalent uranium in the apatite structure has recently been questioned by SERBRYAKOVA and RASUMNAYA (1962).

**DISCUSSION**

Some conclusions as to the probable evolution of the deposit in recent times can be drawn from the surface distribution of the phosphorites. Concentrations vary locally but from its subaerially exposed to its submerged parts, the deposit forms a continuous unit with sharp boundaries offshore as well as onshore. The influence of the previously existing drainage on the dispersion of the phosphorite over the present shelf is evident. The deposit ends abruptly north of Bahia San Juanico beyond which no gully exists along the coast, while it fans out in front of the bay where the five major stream channels reach the shoreline. The control may be only partial and must not be recent as concentrations increase with depth and the richest lense is well offshore. To the west also, a sharp decrease in concentration exists everywhere at about 100 m, the approximate depth at which the platform should have been exposed during the last glacial low. The deposit represents a sandy facies: it is not associated with the fine reducing muds deposited on the outer shelf or with the calcarenite oozes present on the offshore banks, as could be reasonably expected if apatite deposition were directly related either to recently accumulated organic matter or carbonate diagenesis in areas of little deposition. In all samples the intensity of reworking undergone by the deposit is indicated by a close parallelism in grain-size frequency distribution and sorting between the phosphatic and non-phosphatic sand-size fractions. Offshore and beach materials are very similar in these respects,
which suggests that beach processes may have played a considerable role in modeling the present distribution.

The area of occurrence is an erosional platform: Pliocene and Pleistocene horizons have vanished and may have been reworked into the phosphate bearing sandy cover of variable thickness found regionally above the Miocene unconformity. That these served as a source of at least some of the phosphorites is suggested by the presence of a fossil phosphatic brachiopod of corresponding age in close association with the phosphorite bearing sands. If so the deposit would be residual either in part or totally and date back to some previous marine transgression of the present platform in Pliocene or Pleistocene times. General physical conditions then may not have been unlike those found now, since climatic fluctuations along the coast of California appear to have been minimal since late Miocene (Durham, 1950) and no major diastrophism modified Baja California during the same period (Durham and Allison, 1960). Whatever the exact period of occurrence, phosphate deposition was not confined to the shelf off Santo Domingo but must have been widespread regionally as phosphorite grains are present in small quantities in the beaches of Viscaino Bay to the north.

Possible effects of former changes in sea level are obscured by the transformations suffered by the deposit during the last transgression. In the course of this event, the phosphorites appear to have been carried down over short distances to the temporary shoreline by local streams and incorporated into subsequently submerged beach deposits. Longshore transportation in recent times has carried to the south voluminous masses of this originally Plio-Pleistocene material filling up the present lagoons and causing a general progradation of the coastline. The irregular knobby surfaces of the grains somewhat suggestive of growth also indicate that they were subject to little mechanical wear after leaving their formation sites.

In the present state of evolution of the deposit, the phosphorite-rich sediments of the central shelf at 50 m. or more depth are within a quiet environment of little to no deposition in which further mineralisation may take place, while the large fraction of the deposit now in the nearshore and on the beaches is undergoing reworking and temporary burial. This situation may be expected to have lasted 5,000 years or more and some increments of the deposit could be expected over the shelf during this interval. However, from examination of the sediments, the deposition of phosphorite on the central shelf does not seem significant at present either because of very slow rates or because the conditions are not fulfilled. If diagenesis of carbonate minerals such as the phosphatization of foraminiferal tests is the process by which the phosphorites develop, no material suggestive of this transition is observed except at places along the banks and on the upper continental slope. On the other hand if the phosphatic pellets form by accretion, this mechanism is not indicated by the sharp cut-off of the phosphorite grain-size distribution toward the small sizes and must scarcely take place on the surface of the existing pellets since silica occurs at the periphery.

An interpretation of the \(^{14}\text{C}\) ages obtained is difficult as they represent inte-
grated averages over the entire period of deposition. In order not to contradict the observations, apparent ages between 10,000 and 20,000 years could only be explained by assuming that present additions of apatite are taking place at the surface of apatite grains inherited from Pliocene or Pleistocene beds. If this recently deposited apatite had the same mean carbon activity as the surface water off California (14.1 d.p.m./gC; G. Bien, personal communication, 1962), it should represent approximately 30% by weight of sample No.2 and about 10% of sample No.3 (Table II) to explain the respective ages of the samples. If apatite deposition were taking place at this rate, it seems that it would not escape observation.

The present rate of supply of phosphate to the sediments also supports the view that the deposit has required more than a few thousand years to accumulate. In some instances the deposition of apatite in marine sediments has been clearly shown to occur above and not below the sediment–water interface (Goldberg and Parker, 1960). In the present case, however, the surface area of pellets exposed to the bottom waters represents only a small fraction of the total surface area of the deposit and except near the surf zone, overturning of the sediment layer does not easily take place. Thus interstitial deposition of phosphate regenerated within the sediments is likely to be more important than direct precipitation from sea water. At the present rate of supply of organic matter to the sediments, at least one half to one million years appears necessary to build up adequate reserves. Taking into account the kinetics of mineralisation and several intervals of emergence of the platform, the total time involved in forming the deposit may be closer to two or three million years. Inevitably periods of active buildup must have been followed by cycles of reworking, temporary burial and diagenesis.

The usual lack of internal symmetry of the pellets and the random intermixing of the apatite with clay and coarser clastic particles suggest that growth around nucleating centers has been rare. The fabric of the pellets is more suggestive of crystallization of apatite in interstices within sediment grains previously held or not in cohesive structures: fecal pellets, mud fillings of microinvertebrates skeletal remains etc. The migration of phosphate and its concentration into colloid forms may be involved (Kasakov, 1950), but the frequent position in thin sections of apatite crystallites around cloudy opaque zones would imply that the phosphate is normally derived from nearby organic matter. The association of silica and apatite is an important feature of the deposit. It has been reported elsewhere (O'Brien, 1953; Arrhenius, 1960). Both the silica and the phosphate could have been supplied by plankton remains accumulating from local waters. The silica appears concentrated at the periphery of the pellets as if partial segregation of the two materials had taken place. It may be that the silica-rich envelopes around the pellets are the end-products of the deep alteration of foraminiferal tests in which the calcium carbonate served as an initial surface of deposition for calcium phosphate, later replaced by opaline silica.
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