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ECONOMIC DEPOSITS OF THE CALIFORNIA OFFSHORE AREA

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During recent years marine sediments have attracted ever increasing attention, because certain types that contain appreciable amounts of valuable metals and minerals could become commercial sources of industrial raw materials in the near future. To best discuss the economic aspects of the mineral deposits that lie on the sea floor off California, it is preferable to divide the ocean bordering the State into three general geographic regions: the beach and nearshore area, the continental shelf and slope, and the deep-sea floor. Mineral resources in all of these regions are considerable and are virtually untapped.

The beach and nearshore areas of the California coast are favorable zones for the occurrence of black sand and precious metal placers. The continental shelf and slope are known to contain authigenic materials of commercial interest such as glauconite and phosphorite, as well as sizeable reserves of petroleum and natural gas. The deep-sea floor contains extensive deposits of manganese and other metals in the form of nodules. Of all of these potential mineral resources available from the oceanic area off California only one, petroleum, is being recovered on a large-scale basis today.

BEACH AND NEARSHORE PLACER DEPOSITS

The world contains many commercial beach placers that have been mined for their heavy mineral content for generations. While the average concentration of heavy minerals in marine placer deposits is usually low, the combination of modern dredging techniques and low-cost beneficiation has greatly expanded the amount and variety of occurrences that can be considered economic resources. Heavy mineral deposits found on present beaches are part of the marine environment because they lie within the influence of the ocean and are continually reworked and enriched by surf action. In addition, many modern beach deposits represent only the small land-exposed border of a large mineral-bearing zone that extends seaward several miles.

The principal deposits along the ocean beach, and in submerged beaches, are a result of the natural concentration of minerals in sands that have been carried to the ocean by streams or that have resulted from the cutting back of sedimentary bluffs by waves. The winnowing action of the surf forms erratic and changing deposits, which take the shape of lenticular beds, or, more commonly, thin layers of concentrated black sand interstratified with layers of gray sand. The

greatest accumulation of valuable minerals is usually found on the landward side of these deposits where the wave action was strongest. All placer deposits vary somewhat in appearance and configuration, however, marine placers tend to be individually larger, and may be even higher in grade, than many dry-land placers.

The present beaches of the State of California are known to contain many zones favorable for heavy mineral accumulations, and in fact, several beach areas have been mined intermittently for many years. Early-day miners were limited to low-tide operations; however, present technology places large portions of the State's submerged lands in the category of available prospecting ground. Concentrations of placer minerals may be found as far seaward as 300 to 400 feet below the present sea level on the continental shelf of California. The repeated changes in sea level during Pleistocene time, and the low stands that were attained, resulted in exposure and subsequent erosion of much of the inner shelf of California. Rivers discharging into the ocean at that time would have cut canyons and formed placers in areas seaward of the present shoreline and developed beaches along the then existing strandline.

Marine placers usually contain concentrations of heavy, tough, chemically resistant minerals; the most abundant of these minerals found in California waters are probably magnetite and ilmenite. The largest quantities of both of these have been derived from the erosion of the ferromagnesian rocks of the Coast Ranges and their related sediments. Less abundant, but nonetheless commonly associated with these black sands, are gold and the platinum group metals, and many of the inert oxides and silicates such as chromite, rutile, zircon, monazite, uranoan thorite, garnet, and gemstones. Relatively insoluble sulfides such as cinnabar have also been recovered in small amounts from the beach placers of California.

Black sands of the Pacific coast have been exploited periodically since the 1870's, originally for gold and platinum but more recently for iron and titanium. During early periods of mining activity, the richest and most successful deposits were worked at a good profit. From that time onward, however, other ventures that have attempted to recover minerals from beach sands have not proven as successful.

Most of the titaniferous magnetite mined in California has been produced from Los Angeles County, and beach sands recovered from Redondo and Her-



Photo 1. Beaches are interesting areas in which to prospect for mineral deposits. Not only is much of the processing done by the crushing, grinding, and concentrating action of the ocean surf, but the beaches are frequently of overwhelming beauty.

mosa Beaches supplied a large part of this production. The placer deposits occur between Redondo Beach and Palos Verdes Point, covering about 2½ miles of beach. In this placer are found some concentrations of almost pure ilmenite and magnetite, in a 3:2 ratio. The valuable placer minerals occur in lenticular bodies of heavy sand that are about 5 feet thick, 100 feet wide, and 150 feet long. Near Clifton a sand worked in 1927, was reported to contain 20 percent "titaniferous iron" and magnetite, with a residue of quartz, olivine, epidote, garnet, and zircon (Tucker, 1927, p. 287).

A beach deposit farther north near Aptos, in Santa Cruz County, has been worked periodically for its titanium and iron content by several companies. Of these, the principal consumer was Triumph Steel Co., which utilized the sands for producing sponge iron, alloy steel, and briquetted magnetite by a unique smelting process. The early mining at Aptos Beach, however, was for gold, but it was reportedly unsuccessful. These black sand placer deposits occur in both the present beach and in older marine terraces away from the shoreline. The sands contain magnetite, ilmenite, chromite, garnet, zircon and quartz. Irregular crescents of black sand, 100 to 200 feet long and as much as 50 feet wide, that occur along the foot of sandy bluffs are said to be mostly magnetite, with some martite, and enough ilmenite to assay 16 percent TiO_2 .

Black sand concentrations occur in beaches at quite a few other locations along the California coast, and many have been sampled or mined periodically in search for gold. Some amounts of gold have been recovered from beach sands in Humboldt County, particularly at Gold Bluff where occasional high values of gold and small amounts of platinum have been found with magnetite and chromite sands. Beach sands near the Oregon border in Del Norte County contain high concentrations of iron and chromium minerals. One sample of sand from this area assayed 480 pounds of magnetite, 210 pounds of chromite, and 56 pounds of monazite per ton, and also contained a small amount of gold. Most placers containing unusually large amount of chromite are found along the northern coast of California, however, an extremely high-value sample of chromite, running over 1,000 pounds per ton of natural sand, was reported to have been taken from the beach in San Mateo County.

High concentrations of garnet occur in the beach deposits near Fort Bragg, in Mendocino County, and at Point Sal, in Santa Barbara County. The garnet found in beach deposits is generally too fine to have commercial value as an abrasive; however, small quantities have been sold for other purposes.

No known concentrations of monazite sand of present commercial importance exist in California, although sands near Crescent City in Del Norte County have

been found to contain economically significant, but sporadic, accumulations of monazite.

Uranium minerals occur in small quantities in some beach alluvial deposits, but no commercial amounts have been discovered. A few years ago, uranoan thorite was discovered along the beach between Half Moon Bay and Monterey. A ton of sand taken along these beaches will yield one pound of uranoan thorite which contains 7 percent uranium oxide; a concentration too low to be commercial (Hutton, 1959, p. 80-90). More recent studies have shown the range of thorite occurrences in beaches and offshore areas to extend north beyond San Francisco.

Diamonds are occasionally found as a mineralogical curiosity in the beach sands of San Mateo County, and also reportedly in Humboldt County. Typically, the diamonds are in the form of highly irregular fragments and nowhere are they concentrated enough to have commercial value.

Jade is the only gem material known to occur in recoverable quantities in California beach deposits. Nephrite jade was discovered in the late 1930's along a 2-mile stretch of coast in southern Monterey County, midway between Morro Bay and the City of Monterey. Some excellent quality nephrite has been collected on the narrow pebble beach in what has become known as the Jade Cove area. Gem material ranging in size from small pebbles to large beachworn boulders have been found, but while many of the pebbles forming the beach are composed of nephrite, only a few of these were found to be of desirable color and translucency. Later, pods of nephrite jade were found to crop out in place along the sea cliffs that border the beach. In the cliffs gray schists and mylonite predominate, and many intrusions of peridotite, now serpentine, have altered the schists forming the bedrock nephrite, which is always near such bodies of serpentine. Chances of finding alluvial concentrations of nephrite in offshore gravels are very favorable. Jade is also believed to occur off the coast of southern California at Laguna Beach, as a sizeable block of this material was reported to have been recovered by skin divers.

A small but important part of the total sand and gravel output of California comes from beach and nearshore sand deposits. Although beach deposits consist mostly of well-sorted sand of fairly uniform composition, gravels of a type used for construction purposes are normally absent in shoreline areas. Deposits from which specialty sands are mined are even less common than those containing aggregate-grade material. Beach sands derived from granitic rocks and notably rich in quartz occur at several places south of San Francisco along the present coast and are mined both for specialty products and aggregate.

Most aggregate sand material recovered from beach deposits is obtained from the sands that rim Monterey Bay from Sunset Bay in Santa Cruz County to the City of Monterey for a distance of more than 30 miles.

In these modern beaches that border Monterey Bay the sand sizes and compositions vary considerably with location, consequently, not all of the sand is of commercial interest and only those containing coarse sand have been mined. Because wave activity varies continually, the average grain size at any given beach changes from time to time, especially with the seasons.

In late 1965 four companies operated five modern beach deposits and one older beach deposit (Hart, 1965). The coarse beach sand that is mined is used mainly for aggregate in plaster, concrete, asphalt paving material, and as sandblasting sand. Small amounts are used for filter sand, roofing granules, foundry, and engine sand. Modern beach sand reserves are difficult to determine because of erosion and depositional action, but in recent years several operators report that their beaches are retreating. Shore erosion in the vicinity is considered by the Beach Erosion Board to be severe, and this problem is under study. Development of offshore sand reserves may provide a solution and lead to restoration of the storm-destroyed beaches for recreational and residential, as well as industrial, purposes.

On the western margin of Monterey Bay, near Pacific Grove, fine white beach sands are being utilized for glass manufacture, and for ceramic, abrasive, and refractory uses. As early as 1867, some of these deposits were worked for the production of glass. The deposits near Pacific Grove, which are derived from the abrasion of granitic rocks, are unlike any other beach sands in California because of their uncommonly white color, and general lack of clay, iron-bearing materials, and rock fragments. They consist of about 53 percent quartz grains, 46.5 percent feldspar, and 0.5 percent other minerals including biotite, ilmenite, garnet, zircon and monazite. Nearly all of the sand grains of this deposit will pass through a 20-mesh sieve.

No commercial operations to recover calcareous sands from the shelf areas of California have been

attempted. However, Recent deposits of shells and mud, dredged from San Francisco Bay, provide the principal raw materials for a portland cement plant at the Port of Redwood City.

PETROLEUM

Petroleum is the mineral resource that occurs in the waters adjacent to the California coast having the greatest present value and the most promising potential for future large-scale increase in production. Oil fields along the California coast are localized in deep sedimentary basins containing sharply folded rocks. Great quantities of oil have been found in the relatively small basins of Los Angeles, Ventura, and Santa Maria, but elsewhere in the coastal region only small pools have been developed. Productive basins are normally at an angle to the general trend of the coast, and they extend westward some distance beyond the shoreline out under the Pacific Ocean. These submerged areas are excellent prospecting grounds for potentially large petroleum and natural gas resources.

While much oil has been produced from offshore wells in California, there is still a paucity of general geological knowledge of the subsea floor in most areas of the State; an exception is the part of offshore southern California situated south of Point Conception. Rocks of this province consist of schist and granitic basement, of Jurassic age or older, overlain by Cretaceous and Tertiary sediments. Cretaceous and Eocene rocks are exposed over a small percentage of the province, generally on or near islands along the shelf. Oligocene rocks are not known to be exposed on the sea floor; however, oil wells have penetrated such rocks in several places beneath the shelf off Santa Barbara and Ventura Counties. Miocene rocks, widespread petroleum producers on land, are believed to be common offshore, but rocks younger than Miocene are scarce. Pliocene formations have been encountered in several offshore wells in both the Los Angeles and

Table 1. Mineral deposits of the sea

Source area	Minerals of interest
Sea water	Common salt, magnesium for metal and magnesium compounds, bromine, potash, soda, and gypsum—potentially, sulfur, strontium, and borax. Many other elements can be found in sea water; however, processes fundamentally different from those now used would have to be developed in order to extract these elements.
Marine beaches	Placer gold, platinum, diamonds, magnetite, ilmenite, zircon, rutile, columbite, chromite, cassiterite, scheelite, wolframite, monazite. Quartz, calcium carbonate, and sand and gravel.
Continental shelves	Calcareous shells, phosphorite, glauconite, barium sulphate nodules, sand and gravels; placer deposits of tin, platinum, gold, and other minerals in drowned river valleys.
Deep-sea floor	Clays suitable for structural uses, possibly also as a source of alumina, copper, cobalt, nickel, and other metals. Calcareous oozes for cement rock and other calcium carbonate applications. Siliceous oozes for silica and in diatomaceous earth applications. Animal remains as a source of phosphates, and possibly certain metals such as tin, silver, lead, and nickel. Zeolites as a source of potash. Manganese nodules as a source of manganese, iron, cobalt, nickel, copper, molybdenum, vanadium, and perhaps other elements.
Rocks beneath subsea floor	Oil, gas, sulfur, salt, coal, iron ore, and possibly other mineral deposits in veins and other forms as in the rocks on land.

Ventura basins, and are probably more common on the shelf than indicated by surface samples on the sea floor (Calif. Div. Mines, 1959).

The sub-sea area of central and northern California is, of course, far less known geologically and topographically than is the rest of the State. From an economic viewpoint, two-thirds of the California coast is bordered by Tertiary and Cretaceous rocks having oil-producing potential. Two of these sedimentary regions, the Los Angeles and Ventura basins, have already yielded a great amount of oil and gas from their offshore portions, and undoubtedly a substantial proportion of their reserves still remains to be discovered. Probably, the most favorable sedimentary basins that extend into adjacent shelf areas from land are the Santa Maria basin of Santa Barbara and San Luis Obispo Counties, and the Eel River basin of Humboldt County. However, other favorable ground that is not an extension of onshore basins surely exists. Potentially petroliferous zones lie offshore from the sedimentary sequences of Marin, Sonoma, and southern Mendocino Counties.

The California coast is the scene of rapidly increasing offshore activity because of the State's growing demand for fuel, the development of technological skills to drill and operate in extremely deep water, recent successes in the Ventura basin, and Federal offshore lease sales in northern California in the past two years. The Federal decision to open for oil exploration more than 1,000 square miles of offshore acreage beyond California's 3-mile limit makes this region the best remaining block of wildcat territory in the Nation. Much of the area represents the seaward extension of the Los Angeles basin, which has produced 40 percent of California's oil and is the world's most prolific basin in terms of established reserves per cubic mile of sediment.

Los Angeles basin activity has become enhanced by significant extensions of the Huntington Beach field and by the solution of legal problems involving development of the East Wilmington field. East Wilmington field is the largest undeveloped known oil reserve in the United States, containing an estimated 1.2 billion barrels of recoverable oil. Five companies have won 80 percent of the field by offering 95.56 percent of net profits as royalty. Building of four 10-acre drilling islands is underway and production is expected to reach 200,000 bpd within a decade.

The Ventura basin has seen considerable offshore development in recent years. This activity continues with the report of a new field recently discovered offshore from Carpinteria. In addition, new gas reserves have been developed off the Santa Barbara coast and directional drilling is underway from beach locations at Gaviota.

The first wildcat ever drilled in Federal waters off the State was completed in 1964 just north of San Francisco in the Point Reyes area. The hole was drilled in 360 feet of water and was taken to 4,400 feet with

inconclusive results. A second hole is now being attempted in the same general location.

In 1965 a wildcat was being drilled north of Santa Barbara, off Morro Bay, in 630 feet of water on Federal lands beyond the 3-mile limit. While drilling in this depth of water may seem amazing, oil companies now feel that it is feasible to drill throughout the year in California in places where the water is as deep as 1,000 feet.

TAR DEPOSITS

Unusual occurrences of submarine tar deposits have been observed in shallow water on the sea floor off southern California in at least three localities; the Point Conception area, Coal Oil Point near Goleta, and off Carpinteria (Vernon, 1963). Scuba-diving geologists mapping underwater for oil companies first discovered these tar deposits in the mid-1950's. Although the potential economic importance and true extent of the deposits is unknown, it is believed that tar recovery could be accomplished by known mining processes if the deposits prove to be sizeable.

Tar is most abundant in the Point Conception area where a sheet of the material covers at least one-fourth square mile and forms a 10- to 12-foot scarp at its seaward edge. East of the Point, individual deposits that range up to 100 feet in diameter and 8 feet in height have been reported.

The deposits are irregularly distributed along the east-west trend of faulted anticlines exposed in shale outcroppings on the ocean floor. Most of the tar occurs in mounds that have roughly circular outlines and resemble miniature volcanoes with sides sloping gradually upward toward a vent at a central high point. The mounds are essentially discrete masses of tar in the form of flows. Fresh material is being extruded continuously from the vents of most mounds, and a whiplike strand of fresh tar is commonly found floating above the central vents. Rotary cores taken near one group of tar mounds show that the tar fills fractures in the shale to a depth of 10 feet, but below this depth the fractures in the bedrock are essentially free of tar.

Studies of the tar deposits indicate that Late Quaternary fluctuations in sea level uncovered the site of the tar deposits and wave action removed previous accumulations, and probably also removed several tens of feet of shale forming the surface on which the mounds are now accumulating. It is suggested that the present deposits must have developed since the last major rise in sea level, about 9,000 years ago.

BARITE DEPOSITS

Limited deposits of barite concretions have been found embedded in marine mud at depths between 2,000 and 2,400 feet along the northeast side of San Clemente Island off the coast of southern California. About 250 loosely mixed concretions, along with about 100 kilograms of green mud, have been dredged from this area. They are irregularly shaped nodules, and range from 1 to 25 cm in length. Chemically and min-

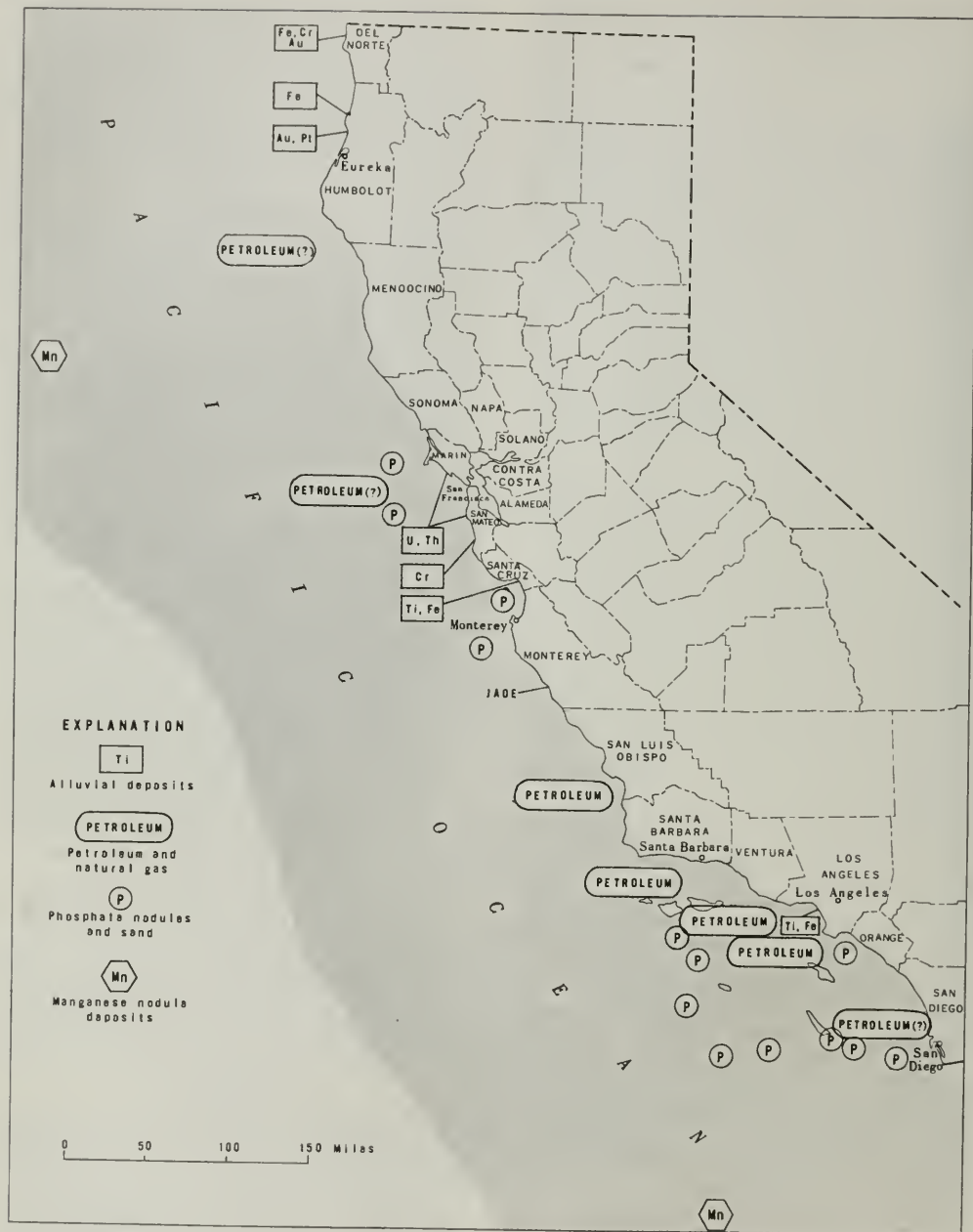


Figure 1. Sketch map showing the California offshore area and the location of various types of mineral deposits found therein.

erologically they are similar to other barite concretions found on land or recovered from the sea floor. Barium sulphate is present in the nodules in amounts from 62 to 77 percent.

It is believed the barite concretions originated by a reaction between hot solutions ascending along a fault and the interstitial seawater of the sediments (Revelle and Emery, 1951, p. 707). This suggestion is supported by the fact that all known nodule localities are situated on or near large faults, which could have provided an avenue of escape for the hot barium-bearing solutions. It appears likely that the deposits of barite concretions are quite localized, and they should not be considered a potential offshore resource.

GLAUCONITE

Glauconite is an authigenic sea-floor mineral of potential economic interest that is found in widespread occurrence off the Coast of California. This mineral contains from 2 to 9 percent K_2O and could serve as a future source of potash and soil conditioner for agricultural use, or as a source of potassium or potassium salts. Compared to continental deposits of potash salts, marine glauconite sediments could not be considered a rich source of supply, however, mining costs would be relatively cheap and mechanical concentration might possibly produce a product with a significant amount of contained potash.

Glauconite is widely distributed in the terrigenous sediments off the coast of the State, occurring in water depths ranging from 100 to 200 fathoms. The highest concentrations of glauconite occur in environments in which detrital sedimentation is slow or virtually absent, such as banks, ridges, and upper slopes of basins of the continental shelf. Distribution of the mineral is normally patchy both laterally and vertically.

Deposits of glauconite are either *in situ*, having been formed where they now are found, or else reworked, having been transported into the environment in which they are found. Transported glauconite can be recognized because it is usually characterized by fine grains, some of which show evidence of fragmentation. Individual grains of glauconite found in marine muds are in some places as large as 3 mm, although normally they are much smaller. Glauconites off California range from dark green illitic types to pale and yellowish-green montmorillonitic types.

Glauconite deposits of offshore California range in age from Miocene to Late Pleistocene. They have been found in abundance in Recent sediments that form the shelf south of Santa Barbara, where they appear to be reworked from glauconitic sediments of Late Pliocene age. Similar, but less extensive deposits of reworked glauconite are present in other areas off the California coast. Both Santa Monica Bay and the Palos Verdes shelf contain vast areas of glauconitic sands of low concentration. The sea area off Monterey Bay contains local sediments at the shelf break that run as high as 40 percent glauconite, and individual

layers in some offshore areas are known to grade as high as 80 percent glauconite (Pratt, 1962, p. 233).

PHOSPHORITE

Authigenic phosphorite is one of the truly important kinds of rock on the sea floor off California from an economic standpoint. It has been shown by recent scientific and engineering studies to offer great potential as a present-day source of chemical raw materials. Extensive deposits of phosphorite are common in many places off the coast, and are quite near to potential areas of consumption and centers of processing and marketing.

Phosphatic concretions were first discovered on the ocean floor by scientists of the famous Challenger Expedition in the 1870's; however, they were not recognized off the California coast until 1937. Since that time many additional locations have been discovered in the State's coastal waters, and in several of these phosphorite has been found to be the most abundant surface rock. Deposits of phosphorite nodules are now known to extend from the coastal waters off Point Reyes, north of San Francisco, southward to the mouth of the Gulf of California, a distance of 1,300 miles. The nodules occur in some places within a few miles of the coast and they extend as far from shore as the inner edge of the continental slope. The greatest depth from which nodules have been dredged is 8,400 feet, while the shallowest is about 100 feet off southern California. The total area that is known or believed to be covered by phosphorite is about 6,000 square miles (Emery, 1946, p. 69). If it is assumed that the nodule layer has an average thickness of one inch, the

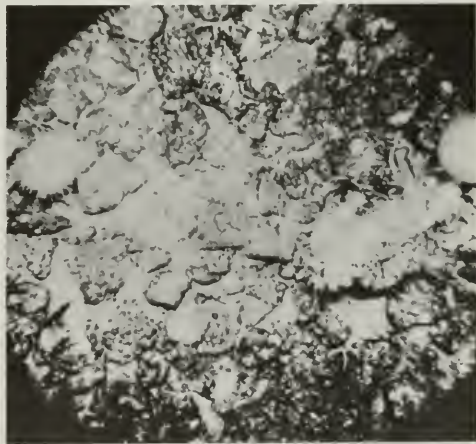


Photo 2. Phosphorite on the Forty Mile Bank area at a depth of 108 fathoms. This photo shows an area of about 16 square feet. The quantity of phosphorite, assuming a monolayer of rock on the surface of the sea floor, is about 500,000 tons per square mile of sea floor. Individual nodules range in size from oolites to blocks with a major dimension of about 2 feet.

region could contain approximately one billion tons of phosphorite rock.

Dredging has indicated that an especially great abundance of phosphorite exists in the continental borderland area of southern California, particularly in the vicinity of Thirty Mile and Forty Mile Banks off San Diego. Deposits have also been identified near Santa Catalina Island, and farther north off Santa Rosa and Santa Cruz Islands. Off central California, phosphorite nodules have been dredged from deposits in Monterey Bay and from the outer shelf in this region as well. West of San Francisco, several hundred pounds of nodules were recovered from dredge hauls in water depths between 400 to 600 fathoms (Chesterman, 1952, p. 366). To the northwest of San Francisco in the vicinity of Cordell Bank, at water depths ranging from 200 to 400 fathoms, over 800 pounds of nodules were taken during sampling. They ranged from 2 to 8 inches in diameter and appeared to be nearly pure phosphatic material. The percentage of sand recovered with the nodules in this region was very low.

Sea-floor phosphorite is known to occur in a wide variety of topographic environments. It has been dredged from the tops and sides of banks and ridges, from deep hills, on steep escarpments, on the walls of submarine canyons, and on the break of the continental slope. Small grains or oolites are common in many inshore areas as well as in the coarse sediment seaward of the main shelf. Most samples of phosphorite, however, have been taken from areas characterized by a slow rate of deposition. In these environments ocean bottom currents are concentrated so that any sediment that reaches the nodules is soon removed and no permanent deposit of fine sediment remains. Sea-floor phosphorite occurs as a veneer or mono-layer covering the ocean bottom for many square miles; no evidence has been found that indicates phosphorites occur to any depth beneath the surface of the ocean floor.

California phosphorites typically occur as nodules and sands, ranging from flat slabs and irregular masses to oolites. They vary in size from small grains of less than 1 mm to nodules well over 3 feet in diameter. Pieces of phosphorite weighing 100 pounds have been recovered in dredge hauls and larger pieces are likely to exist. The nodules generally have flat bottoms and nodelike tops, and their surfaces appear glazed as they are normally coated with a thin film of manganese oxides. From place to place nodular phosphorites vary in color from light brown to black; those from a particular area typically have a group resemblance.

Internally, the nodules display a wide range of structures and purity. Most small nodules have a very fine grained texture and a homogeneous composition, while most of the larger nodules contain some nonphosphatic material, usually composed of sand and glauconite and fragments of nearby bedrock. Frequently, phosphorite forms a thin coating on fragments of local rocks that are lying on the sea floor. In places old-

appearing nodules are cemented together to form a conglomeratic mass. The majority of sea-floor phosphorite shows signs of internal layering either visually or microscopically. These layers are irregular and nonconcentric, and vary in thickness from less than a millimeter to a few centimeters.

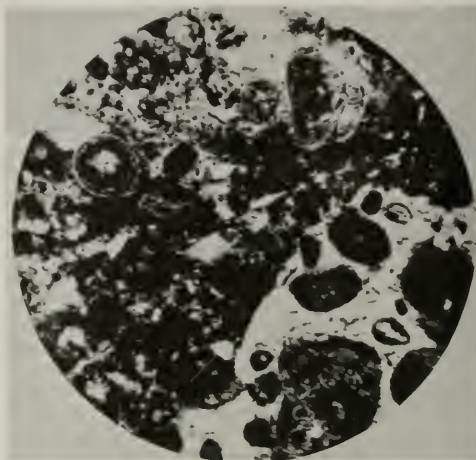


Photo 3. Photomicrograph of a thin section of phosphorite from Forty Mile Bank, showing the oolitic structure of these nodules (x 50).

Sea-floor phosphorites are firm and dense, with a specific gravity of 2.62 and a hardness of 5 on the Mohs' scale. Chemical and mineralogical analysis has proved the nodules to be composed almost entirely of collophane, a nearly isotropic fluorapatite. Associated with collophane in minor amounts is francolite, also a carbonate fluorapatite mineral. Chemical analyses indicate that sea-floor phosphorite is nearly the same composition as reported for deposits of land phosphorites in the United States and elsewhere. It generally contains 20 to 31 percent P_2O_5 and can be upgraded by physical processing to contain 32 to 34 percent P_2O_5 (Mero, 1965).

The process of formation of these unique blanket deposits of nodular phosphorite is still unknown. The evidence available strongly suggests that most of the phosphorite originated as a primary or syngenetic mineral formed *in situ*. Deposits of nodules are most abundant along coasts where there are great and rapid changes of temperature resulting from the meeting of cold and warm ocean currents. In these areas, large numbers of pelagic or deep-water organisms are killed by temperature changes and may accumulate to form sizeable layers of decomposing phosphatic matter on the ocean bottom. In areas where there are large amounts of decaying phosphatic matter, an environment that allows the phosphate to dissolve in sea water is created. The dissolved phosphate migrates

away from this area into the prevailing oxidizing environment of the ocean, and is precipitated in colloidal form. Under certain conditions these phosphate colloids can agglomerate to form nodules.

Another suggested origin is that the phosphorite is precipitated from sea water in areas of strong upwelling ocean currents. In these areas where cooler deep water containing a high concentration of phosphate ions and other nutrients rises to the surface the sea water undergoes an increase in pH and temperature and a decrease of pressure. Carbon dioxide, which serves to hold phosphate in solution, is released. This combination of events serves to explain the modern occurrence of phosphorite in the oxidizing environments of waters along California and other coasts, at least some of which are also areas of upwelling.

Many fossils are found incorporated in the phosphorite nodules. They range from bones and teeth of fishes to sponge spicules and tests of Foraminifera. Of these the Foraminifera are by far the most abundant in the phosphorite, and they are quite useful in determining the age of formation of the deposit. Foraminifera in the California nodules fall into two general groups: middle and late Miocene types in dark brown, older-appearing nodules, and late Pliocene to Recent types in the matrix of light brown forms. Evidence indicates most nodules formed during Miocene time; however, subsequent exposure of nodules on the sea floor may have provided nuclei for renewed Quaternary deposition of phosphorite.

Although phosphatic pebbles are found in the sedimentary strata in some land areas of California (see Dickert, this bulletin), no deposit of rock phosphate within the State has yet proved economic to mine. It appears likely that if offshore deposits of phosphorite prove to be sufficiently extensive, they can offer a substantial source of low-grade ore. Not all of the phosphorite found off California will be economic to recover, as some deposits are too marginal or too scattered to be profitable and others are too mixed with nonphosphatic rocks or too unfavorably located for commercial recovery. However, if it is economic to mine only 10 percent of the phosphorite speculated to be off the coast of California, there is a reserve for about 200 years of mining at a rate of 500,000 tons per year.

MANGANESE NODULES

The most promising of ocean-floor mineral occurrences found off California are the deep-sea deposits of manganese nodules. Nodular manganese as a pelagic sediment is probably one of the most common forms of hard rock found at the surface of the lithosphere, but although its existence has been known since the 1870's, its potential economic significance was not apparent until widespread dredging in the Pacific Ocean during the International Geophysical Year revealed its vast extent. The amount of nodules on the Pacific Ocean floor alone has been estimated to be in excess

of 1.5 trillion tons. Furthermore, recent engineering studies on the mining of nodules from the sea floor suggest that such operations may be both technically and economically practical.

Concretionary deposits of ferromanganese minerals are found ubiquitously spread over the ocean bottom where oxidizing conditions prevail at the sediment-water interface. It has been estimated that between 20 and 50 percent of the deep-sea floor in the southwestern Pacific is covered with these concretions, and although their relative abundance in the northeastern Pacific is not yet as well known, sporadic dredging has indicated several potentially large and highly concentrated deposits.

Ocean-floor manganese minerals are most commonly found as loose-lying concretions or nodules at the surface of soft sea-floor sediments. The manganese nodules range in color from light brown to earthy black, are friable with a hardness that does not exceed 3 or 4 on the Mohs' scale, and have a density of from 2.1 to 3.1. On an ocean-wide basis, they have an average diameter of 3 cm; however, they locally vary in size from 1 cm to 25 cm with a few that are even larger. One extremely large nodule recovered from the Pacific weighed 1,700 pounds.



Plate 4. Manganese nodules from the north Pacific, illustrating a few of the many shapes they assume in their growth process. The location data for the individual nodules are: A.) N. 29° 58', W. 125° 55', depth 4,325 m.; B.) N. 23° 17', W. 138° 15', depth 4,890 m.; C.) N. 22° 30', W. 113° 08', depth 3,600 m.; D.) N. 14° 11', W. 161° 08', depth 5,652 m.; E.) N. 9° 57', W. 137° 47', depth 4,930 m.; F.) N. 21° 27', W. 126° 43', depth 4,300 m.

In physical appearance, the nodules exhibit a variety of shapes, such as marbles, tablets, potato shapes, cylinders, slabs, and irregular masses. Nodules from different parts of the ocean generally have unique physical characteristics, but those within a given deposit show a group resemblance. Their external form commonly depends on the shape of the nucleus. Some, however, show several nuclei because growing nodules have coalesced to form slab-like concretions with multiple knobs. (See photo 4.)

The mineralogy of the nodules is complex. As a number of distinct minerals are generally present the nodules may be classified most appropriately as rocks. In addition to the common detrital silica and alumina minerals, such minerals as opal, rutile, anatase, barite, nontronite, goethite, and at least three manganese oxide minerals of major importance have been recognized in the nodules. Generally these minerals occur as intimately intergrown crystallites. Grutter and Buser (1957, p. 132) found that the structure consists of layers of MnO_2 in an irregular pile of quasi two-dimensional crystals. Their X-ray diffraction pattern is of a type similar to that of the mineral lithiophorite. They suggest a structure of two MnO_2 layers, 10 Å apart, separated by a layer consisting of $Mn(OH)_2$ and $Fe(OH)_3$, and possibly sodium ions. Many of the nodules contain more iron than can be accommodated in the in-between hydroxyl layer and the excess iron appears in the form of goethite. The in-between layer seems also to accommodate a group of cations, such as nickel, copper, cobalt, and zinc, which may be found in rather high concentrations.

Several hypotheses have been suggested concerning the formation of the nodules. The most plausible inorganic theory of formation, as based on presently available data, begins with sea-water saturated with manganese and iron, which has been derived largely from streams, continental erosion, and volcanic eruptions. With the evaporation of the sea water at the ocean surface, manganese and iron are forced to precipitate as colloidal particles, which filter down through the sea water scavenging nickel, copper, cobalt, vanadium, molybdenum and other metals from solution. The manganese and iron sols are swept along by bottom currents and accrete on the sea floor around physical nuclei such as clay particles, organic material, coral, or pumice.

Deposits of manganese nodules appear to occur essentially as a mono-layer on the surface of the deep-sea floor. Some nodules do occur at discrete levels within superficial sea-floor sediments, but they are in less abundance than on the surface itself, at least in the more explored upper meter or so of the sediments. Detailed information on the distribution and concentration of macroscopic nodules on the sea floor has been obtained through bottom photography and by sampling. Crusts and large nodules appear to develop on topographic highs or in areas where there is a low rate of total deposition, probably because in these areas growing nuclei are not so quickly buried by other sedimentary components. In general, the concentration of nodules in individual deposits tends to increase toward the center of the Pacific Ocean. Measurements in the eastern Pacific gave an average nodule

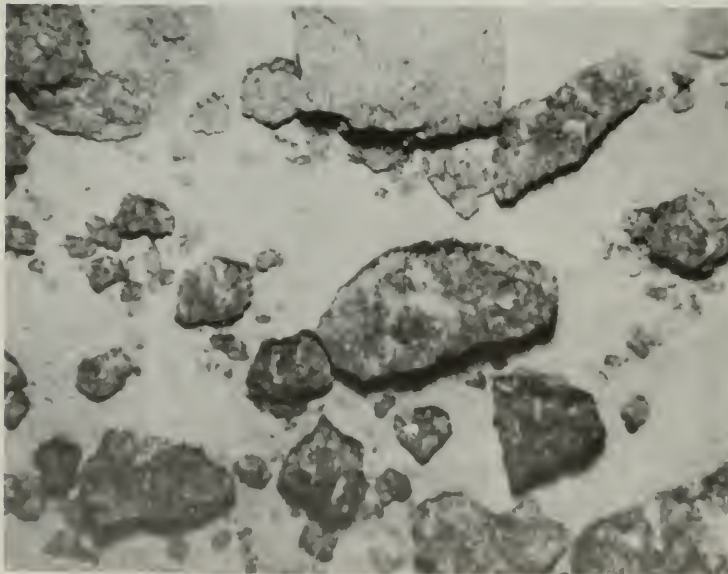


Photo 5. Manganese nodules on the ocean floor at N. 26°, W. 135°, in 4,330 m of water between California and Hawaii. The largest slablike nodule is about 23 cm in diameter. Many of the blocklike nodules in this photo may be only manganese dioxide encrusted blocks of pumice. Photo by Carl Shippek, U.S. Naval Electronics Laboratory, San Diego, California.

concentration of 0.9 gms/cm²; measurements in the central Pacific average 1.8 gms/cm² (Photo 5).

Definite regional variation in the composition of manganese nodules has been observed in the Pacific Ocean. The chemical basis for determining whether a nodule is "high" in regard to the amount of a particular element is rather arbitrary; however, using a detritus-free weight percentage base of about 1 percent for cobalt, nickel, and copper, a geochemical pattern becomes apparent. In the case of manganese, a weight percentage of 40 percent is considered "high", and if the manganese/iron ratio is less than unity, a nodule is assumed to be "high" in iron. In the central part of the eastern Pacific, nodules are found to be "high" in nickel and copper. In the central Pacific, nodules are "high" in cobalt, but contain very little copper. Nodules near the west coast of the United States are characterized by a manganese/iron ratio of less than one and an iron/cobalt ratio that is greater than that of other regions. Nodules from the region that borders the North American Pacific coast have an average chemical composition, on a detrital-free mineral basis, in percent of: iron—28.3, manganese—21.7, cobalt—0.35, nickel—0.46, and copper—0.32.

Although no nodule deposits have been reported as occurring on the continental shelf and slope of California, much manganese dioxide has been found there in the form of coatings around rock fragments. For example, in a seahill area about 30 miles off the coast near San Diego large quantities of manganese dioxide have been reported cementing andesite fragments. Elsewhere off California in deeper water, a considerable number of rocks with manganese crusts have been dredged. These are generally angular slabs and tabular masses with a core of altered pumice fragments, and between the slabs in many places nodules have been found to cover much of the bottom.

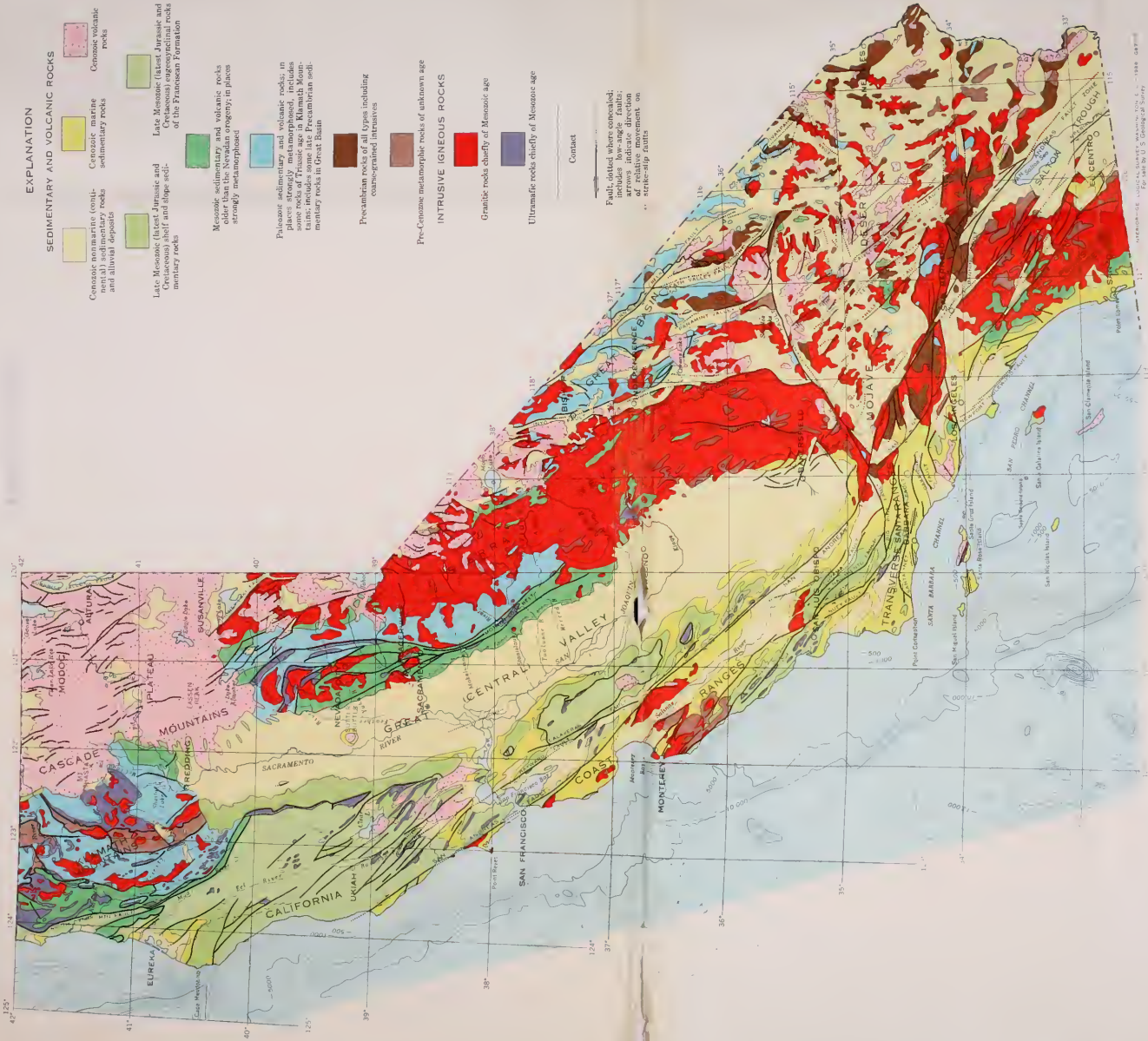
Manganese nodules may occur over an extensive region of the deep-sea floor due west of Cape Mendocino. Samples recovered from as close to the continent

as 250 miles contain approximately 19 percent manganese, 8 percent iron, 0.6 percent nickel, and 0.4 percent copper. From about 680 miles to 2,100 miles west of Cape Mendocino, recovered nodules contain an average of 14 percent Mn, 8 percent Fe, 0.5 percent Ni, 0.4 percent Cu, and 0.28 percent Co. Approximately 2,000 miles west of San Francisco, nodules were found to contain about 20 percent Mn, 14 percent Fe, 0.4 percent Ni, 0.25 percent Cu, and 0.13 percent Co. To the south in a zone 1,000 miles west of Cape San Martin, nodules recovered contained 10 percent Mn, 13 percent Fe, 0.3 percent Co, 0.3 percent Ni, and 0.3 percent Cu. West of Los Angeles, approximately 1,600 miles at sea, a dredge haul retrieved nodules that contained 15 percent Mn, 12 percent Fe, 0.6 percent Ni, 0.3 percent Cu, and 0.3 percent Co. Most of the nodules taken in waters off California occur in a depth range from 4,500 to 5,500 meters.

The feasibility of mining deposits of manganese nodules has been studied in some detail by Mero (1965), and he concludes that a proven engineering system such as drag dredging or suction dredging could economically recover nodules from specific deposits off California. Before seriously considering mining these deposits, however, it will be necessary to learn far more about their environment and occurrence so that the best sites for operations can be selected. Should these deep-sea deposits prove to be ores of various metals, the reserves in the Pacific Ocean are staggering, as the indicated reserves for many of the metals range into quantities sufficient to support mining for hundreds of thousands of years. From a mining standpoint, the nodules rich in cobalt, copper, and nickel are of greatest interest. Maximum concentrations of these metals found in nodules thus far are 3 percent copper, 2 percent cobalt, and 2 percent nickel. Economic incentive may soon provide sufficient information to bring deep-sea nodules into the realm of true ore deposits.

REFERENCES

- California Division of Mines, 1959, *Offshore geology and oil resources: California Div. Mines Mineral Inf. Serv.*, v. 12, no. 5, p. 1-7.
- Chesterman, C. W., 1952, *Descriptive petrography of rocks dredged off the coast of central California: California Acad. Sci. Proc.*, 4th ser., v. 27, p. 359-374.
- Emery, K. O., 1960, *The sea off southern California, a modern habitat of petroleum: New York, John Wiley and Sons, Inc.*, 366 p.
- Grueter, A., and Buser, W., 1957, *Untersuchungen an Mangansedimenten: Chimia (Aarau)* 11, p. 132-133.
- Hart, E. W., 1965, *Mines and mineral resources of Monterey County: California Div. Mines and Geology, County Rept. 5.* (In press)
- Hutton, C. O., 1959, *Mineralogy of beach sands between Halfmoon and Monterey Bays, California: California Div. Mines Spec. Rept. 59*, 32 p.
- Mero, J. L., 1964, *Mineral resources of the sea: New York, Am. Elsevier Publishing Co.*, 312 p.
- Pratt, W. L., 1962, *The origin and distribution of glauconite from the sea floor off California and Baja California: Southern California Univ., Los Angeles, Ph.D. thesis*, 296 p.
- Revelle, R. D., and Emery, K. O., 1951, *Barite concretions from the ocean floor: Geol. Soc. America Bull.*, v. 62, no. 7, p. 707-723.
- Tucker, W. B., 1927, *Los Angeles County: California Mining Bur.*, 23d Rept. State Mineralogist, no. 3, p. 287-313.
- Vernon, J. W., and Slater, R. A., 1963, *Submarine tar mounds, Santa Barbara County, California: Am. Assoc. Petroleum Geologists Bull.*, v. 47, no. 8, p. 1624-1627.



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GEOLOGIC MAP OF CALIFORNIA

COMPILED BY U.S. GEOLOGICAL SURVEY
AND CALIFORNIA DIVISION OF MINES AND GEOLOGY

SCALE 1:2,500,000

0 50 100 MILES

0 50 100 KILOMETERS

0 5000 FEET DATUM 15 SEA LEVEL

1966