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GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

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# Zirconium and Hafnium in the Southeastern Atlantic States

By JOHN B. MERTIE, Jr.

CONTRIBUTIONS TO ECONOMIC GEOLOGY

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# TABLES

# ZIRCONIUM AND HAFNIUM IN THE SOUTHEASTERN ATLANTIC STATES

By John B. Mertie, Jr.

## ABSTRACT

The principal source of zirconium and hafnium is zircon, though a minor source is baddeleyite, mined only in Brazil. Zircon is an accessory mineral in igneous, metamorphic, and sedimentary rocks, but rarely occurs in hardrock in minable quantities. The principal sources of zircon are therefore alluvial deposits, which are mined in many countries of five continents. The principal commercial deposits in the United States are in Florida, though others exist elsewhere in the southeastern Coastal Plain.

The evidence indicates that conditions for the accumulation of workable deposits of heavy minerals were more favorable during the interglacial stages of the Pleistocene epoch than during Recent time. Therefore detrital ores of large volume and high tenor are more likely to be found in the terrace deposits than along the present beaches. Other concentrations of heavy minerals, however, are possible at favored sites close to the Fall Line where the Tuscaloosa formation rests upon the crystalline rocks of the Piedmont province.

A score of heavy and semiheavy minerals occur in the detrital deposits of Florida, but the principal salable minerals are ilmenite, leucoxene, rutile, and zircon, though monazite and staurolite are saved at some mining plants. Commercial deposits of heavy minerals are generally required to have a tenor of 4 percent, though ores with a lower tenor can be mined at a profit if the content of monazite is notably high. The percentages of zircon in the concentrates ranges from 10 to 16 percent, and in eastern Florida from 13 to 15 percent. Thus the tenor in zircon of the ore-bearing sands ranges from 0.4 to 0.6 percent.

The content of hafnium in zircon is immaterial for many uses, but for some purposes very high or very low tenors in hafnium are required. Alluvial zircon cannot be separated into such varieties, which, if needed, must be obtained from sources in bedrock. It thus becomes necessary to determine the Hf : Zr ratios in zircon from many kinds of bedrock.

Granitic rocks are the principal sources of zircon, though not the best sources of zircon with a high tenor in hafnium. A general study by the Geological Survey of the granitic rocks of the Southeastern Atlantic States has been in progress for 10 years, and hundreds of samples of granitic accessory minerals have been acquired. Thirty samples of zircon from these collections were selected for spectrographic and X-ray determinations of their tenors in hafnium. Nine other samples of alluvial zircon were included, of which three are from Florida and six

from foreign countries. No domestic zircon was discovered with very high or very low tenors in hafnium.

The volume of zircon in the southeastern Coastal Plain is enormous, but most of it is not recoverable. The minable reserves of heavy minerals, however, are very large, and from these it is estimated conservatively that 10 million short tons of zircon can be obtained. The corresponding amounts of zirconium and hafnium, using the mean Hf : Zr ratio of the deposits in Florida, are 4,868,000 and 112,000 tons, respectively. These reserves could be delivered, if needed, at the rate of 100,000 tons a year.

## INTRODUCTION

The history of the discovery of zirconium and hafnium has been recounted by Weeks (1956, p. 543–545, 848–851) and requires no repetition. According to Rankama and Sahama (1950, p. 38–39), zirconium stands 19th and hafnium 46th in the abundance of the elements in igneous rocks. These elements invariably occur together in nature, and their separation is so difficult that ordinary chemical analyses for zirconium state in reality the sum of zirconium and hafnium. The more significant physical properties of zirconium and hafnium are shown in the following table.

*Physical properties of zirconium and hafnium* [1]

| | *Zirconium* | *Hafnium* |
|---|---|---|
| Atomic number | 40 | 72 |
| Atomic weight | 91. 22 | 178. 50 |
| Natural isotopes | 5 | 6 |
| Principal isotope percent | $Zr^{90}$(51.46) | $Hf^{180}$(35.25) |
| Density | 6. 44 | 13. 3 |
| Melting point ° C | 1, 850 | 2, 000± |
| Ionic radius Å | 0. 87 | 0. 86 |
| Electronic configuration | $\ldots 4d^2 5s^2$ | $\ldots 5d^2 6s^2$ |

[1] The data are compiled from following publications: Weeks (1956, p. 884-885); Sullivan (1957, tables 2 and 4); Forsythe (1956, p. 117, 291, 622–623); Stull and Sinke (1956, p. 234); Rankama and Sahama (1950, p. 794–795).

Zircon and baddeleyite are the commercial sources of zirconium and hafnium, but commercial ores of baddeleyite are available only in the Poços de Caldas region, Minas Gerais, Brazil. Rocks containing zircon, however, are generally distributed throughout the world. A score of other minerals are known in which zirconium and hafnium occur, of which the most important is eudialyte. This mineral occurs at many places, of which the best known are southwestern Greenland and the Kola Peninsula of Russia. No mineral has been found in which hafnium is the principal metallic element.

Zircon and baddeleyite have formulas, respectively, of $ZrSiO_4$ and $ZrO_2$; and taking no account of hafnium, the tenors in zirconium of these two minerals are, respectively, 49.8 percent and 74.0 percent. Frondel (1957, p. 2) lists 27 synonyms and varieties of zircon, and baddeleyite has been described also as brazilite, caldasite, and zirkite. The formula for eudialyte is written as $Na_4(Ca,Fe)_2ZrSi_6O_{17}(OH,Cl)_2$.

Certain characteristics of zircon should be mentioned. Pure zircon is a nonmagnetic mineral that is not held in the strongest electromagnetic field. But some zircon contains ferromagnetic inclusions, causing it to be slightly magnetic; and other zircon is metamict, likewise inducing a weak magnetic susceptibility. Such magnetism causes a loss in the amount recovered in commercial separation. Another characteristic is that much alluvial zircon has a yellowish surficial coloration, caused by the deposition of organic matter. Calcining at 1,200°F burns off this coating and produces a snow-white product.

## GEOLOGIC OCCURRENCE

### BEDROCK SOURCES

Granitic rocks [1] and their derivatives are the principal sources of zircon, though this accessory mineral occurs also in other igneous and metamorphic rocks. Granitic rocks of Precambrian and early Paleozoic age constitute most of the bedrock in the Piedmont province of the Southeastern Atlantic States, and in parts of the Blue Ridge province and the Appalachian Ridge and Valley province. Granitic gneisses are much more plentiful than massive granite.

### HOMOGENEITY AND HETEROGENEITY

The accessory minerals of truly magmatic rocks are essentially homogeneous in composition and character, except for differences that may have resulted from reaction phenomena during their crystallization. Therefore magmatic rocks, provided their source rocks have been completely melted, yield zircon and other accessory minerals that are homogeneous. Zircon, however, has the highest melting point of any granitic mineral; and in the fusion of some preexistent source rock, a magma may result in which all the earlier zircons were not completely remelted. Therefore, even in magmatic rocks, it is possible to have some zircon with inherited heterogeneity.

The zircon of orthogneiss may or may not be homogeneous, depending upon its homogeneity or heterogeneity in the magmatic rock from which the gneiss was derived. But a paragneiss may generally be assumed to have consisted originally of detrital minerals derived from different source rocks. Most of these essential and accessory minerals were recrystallized to produce the paragneiss, which caused them to lose their original sizes, shapes, and compositions. Grains

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[1] The term "granitic rocks," as used in this paper, is intended to designate all granular crystalline rocks ranging in composition from granite and syenite to tonalite and diorite, together with their fine-grained equivalents and metamorphic derivatives, regardless of origin.

of zircon, however, owing to superior resistance to deformation and heat, have commonly not been thus recrystallized and retain most of their original characteristics. Generally, therefore, a paragneiss may be expected to contain heterogeneous zircon, derived from more than one original source rock.

The zircon that occurs in granitized rocks includes a first generation that existed in the igneous, metaigneous, sedimentary, or metasedimentary rock before it was granitized; and this first generation of zircon itself is probably heterogeneous. A later generation of zircon is added during the process of migmatitization. Therefore, granitized rocks are almost certain to contain heterogeneous zircon; and generalizations regarding Hf:Zr ratios, tenors of absorbed radioactive or other elements, and radiometric age determinations based upon the contained zircon, are likely to be misleading.

The recognition of homogeneity or heterogeneity in samples of zircon may or may not be possible. The following seven criteria have been formulated by the writer to aid in the recognition of heterogeneity in the accessory minerals of granitic rocks resulting from a detrital origin or from migmatitization.

1. Rounded outlines of one or more accessory minerals.
2. Variations in the color, size, degree of rounding, and physical properties of any one accessory mineral in a single sample.
3. Unusually high or unusually low tenor in all accessory minerals.
4. Unusually high tenor of some particular accessory mineral in a single sample, perhaps to the exclusion of others.
5. Anomalous relationship among the iron ores, notably the predominance of ilmenite over magnetite, or the absence of all iron ores.
6. Marked variations in the plenitude and character of one or more accessory minerals in multiple samples taken either along or across the regional trend of a granitic formation.
7. The presence of heavy minerals, such as corundum, that are not generally characteristic of the granitic rocks.

No single one of these criteria, not even the first, yields irrefutable proof of the heterogeneity of a granitic rock or its accessory minerals; but if several of them are found to apply, a high probability of heterogeneity is adduced. A discussion of these criteria will not be attempted in this paper. Suffice it to say that the first criterion is the most significant one, particularly for zircon; but the second and fourth are also specially important.

The granitic gneisses of the Southeastern States were known originally as the Carolina gneiss, though more specific names are now being substituted for parts of this complex. Arthur Keith, formerly of the U. S. Geological Survey, stated repeatedly in his folios (1901, p. 2; 1903, p. 2; 1904, p. 2–3; 1905, p. 2; 1907a, p. 2–3; 1907b, p.

2–3; 1907c, p. 2–3; 1931, p. 3) that this granitic group includes both metasedimentary and metaigneous rocks. The criteria outlined above tend to indicate that most of these gneisses are paragneisses, though some have been migmatized. Most of the granitic rocks of the Southeastern States are gneissic or schistose, and the zircon found in these rocks is predominantly heterogeneous. This generalization will serve to dispel the illusion that zircon taken directly from any granitic rock is necessarily homogeneous.

## ALLUVIAL CONCENTRATION

Zircon and other accessory minerals of the crystalline rocks occur in all the valley floors of streams that drain the Piedmont and Blue Ridge provinces. Some of these minerals remain in the fluvial deposits, but most of them migrate downstream and eventually become a part of littoral deposits at or near the strand lines that existed at the time of their formation. Many of these littoral deposits were subsequently modified by the action of winds, waves, and coastwise currents; and locally heavy minerals have been concentrated. Alluvial deposits at or near the present or older strand lines are the principal commercial sources of zircon and other accessory minerals.

The compositions and ratios of the detrital heavy and semiheavy minerals depend partly on their original chemical compositions, partly upon the chemical changes induced by weathering, and partly upon their locations with respect to past and present drainage systems. Zircon from different rocks differs mainly in the content of contained trace elements, of which a number have been identified; but it is almost immune to surficial alteration in temperate climates. Therefore, the principal effects of weathering, transportation, and redeposition are to mix zircons of diverse character derived from many different source rocks. Thus, littoral zircon from the same general region tends to approach a mean composition with only minor differences from place to place.

The older formations of the Coastal Plain have been partly eroded to form the younger ones; and therefore all these formations are proximate sources of heavy minerals. The formations of the Coastal Plain range in age from Cretaceous to Recent; and the Tuscaloosa formation, of Late Cretaceous age, is the basal formation in Alabama, Georgia, and the Carolinas, overlapping the crystalline rocks. Heavy minerals, including zircon and monazite, have been recovered by the writer in panning all the stratigraphic units in the coastal plain of South Carolina and Georgia, from the Tuscaloosa formation to the present oceanic beaches. Zircon, owing to its widespread distribution in the crystalline rocks, is present everywhere. But the older of these formations have largely been covered by younger deposits, so that they are not the most favorable sites for prospecting. Large areas of Pleistocene and Recent deposits, however, are accessible; and such deposits, mainly sands, have provided all the local concentrations of heavy minerals that approach or attain a commercial grade.

Distinct Pleistocene terraces have been recognized by all geologists who have specialized in the geology of the Atlantic Coastal Plain, and Cooke (1945, p. 17, 248; 1954, p. 200–204) now recognizes nine such terraces. The alluvial deposits of these terraces are distinguished from one another, not by lithologic or paleontologic data, but mainly by their maximum altitudes above sea level. Named from highest (oldest) to lowest, these terraces are the Hazlehurst, Coharie, Sunderland, Okefenokee, Wicomico, Penholoway, Talbot, Pamlico, and Silver Bluff. The maximum altitudes of the base levels that characterize these terraces are, respectively, 270, 215, 170, 145, 100, 70, 42, 25, and 6 feet.

The deposits that form the terraces have well-defined upper limits marked by the base levels of ancient shorelines, but have no recognizable lower limits. Hence the thickness of each of these stratigraphic units is indeterminate. Thus, a sand or mineral horizon lying between the upper base levels of the Sunderland and Coharie terraces and at or close to the surface would be of Coharie age. But if a stratum was located at some depth below the surface, within the limits of the same base levels, it might be either of Coharie or older age.

Single terraces and groups of terraces have been correlated by Cooke (1945, p. 17, 248) with the several interglacial stages of the Pleistocene epoch. These correlations have a bearing upon the magnitude and tenor of the mineral-bearing littoral deposits. The more readily accessible sands of the Pleistocene terraces probably were deposited in the interglacial stages, when base levels were relatively high; and these sands covered the deposits of the preceding glacial stages, when base levels were lower. Added to such oscillations of the strand line, a general uplift of the land bordering the Atlantic Ocean has been in progress since Cretaceous time. It also is believed that all the interglacial stages were much longer than the time that has elapsed since the last major retreat of the glaciers. Finally, it seems probable that the interglacial stages had climates that were generally milder than those of the glacial stages or that of post-Wisconsin time. These facts and inferences suggest that the conditions of weathering, erosion, transportation, and deposition of sediments were more favorable for the accumulation of heavy minerals during the integlacial stages than in Recent time. It is therefore to be expected that the largest volume of heavy minerals will be found in the terrace deposits, rather than along the present beaches. The history of placer mining in Florida bears out this interpretation. Small deposits of heavy minerals have been found and worked on the present beaches, but large ore deposits, aggregating tens of millions of tons, have been located only on the terraces.

The larger deposits of heavy minerals are thus related to strand lines that existed in the interglacial stages, but it is not inferred that that they are necessarily marine deposits. The general scarcity or absence of marine fossils is opposed to this interpretation. Some of these deposits may have been formed along oceanic or estuarine beaches, but most of them probably accumulated as outwash fluvial deposits from streams that debouched onto a wide lowland bordering the ocean. Many have clearly been modified by eolian action.

The heavy and semiheavy minerals that have been found in the commercial littoral deposits include ilmenite, leucoxene, zircon, rutile, staurolite, garnet, epidote, magnetite, monazite, sillimanite, kyanite, andalusite, xenotime, green spinel, corundum, hematite, brookite, hornblende, and tourmaline. The principal minerals, and those ordinarily recovered, are ilmenite, leucoxene, zircon, and rutile, though monazite and staurolite are recovered at some plants. The proportions of these minerals are variable, but generally zircon constitutes from 10 to 15 percent of the heavy minerals. Along the east coast of Florida, the range is from 13 to 15 percent. Commercial alluvial deposits of heavy minerals are required to have a tenor of 4 percent unless some mineral of higher value, such as monazite, is present in notable quantity. It therefore follows that such deposits have tenors in zircon from 0.4 to 0.6 percent of the sands. Zircon occurs in the granitic rocks of the Southeastern States in amounts ranging from 0.0001 to 0.1 percent, with an average value of about 0.015 percent. Erosion, transportation, and redeposition as Pleistocene littoral deposits have thus increased the average tenor of commercial deposits about thirtyfold.

The tenors in zircon of noncommercial littoral deposits are notably less. In 1948 the writer took 51 samples of sands from the Pleistocene terraces, of which 39 were from South Carolina, and 12 from Georgia. The samples from South Carolina came from Calhoun, Clarendon, Orangeburg, Williamsburg, Dorchester, Berkeley, Georgetown, and Charleston Counties, all within or adjacent to the lower valley of the Santee River. The samples from Georgia came from Glynn, Brantley, Camden, and Charlton Counties, between the mouths of the Altamaha and St. Marys Rivers. The localities from which these samples came are shown in figure 2 and plate 1 of an earlier paper (Mertie, 1953, p. 15 and 31). The samples from South Carolina represented the terraces from the Hazlehurst to the Pamlico, inclusive; those from

Georgia represented terraces from the Okefenokee to the Pamlico, inclusive.

The tenor in heavy minerals of the samples from South Carolina ranged from 0.02 to 0.68 percent, with a mean value of 0.15 percent. The percentage of zircon in the concentrates ranged from 4 to 43 percent, with a mean value of 18 percent. Hence the average tenor in zircon of the sands was 0.027 percent. The tenor in heavy minerals of the samples from Georgia ranged from 0.08 to 0.96 percent, with a mean value of 0.37 percent. The percentage of zircon in the concentrates ranged from 24 to 50 percent, with a mean value of 33 percent. Therefore, the average tenor in zircon of the sands was 0.12 percent. The three corresponding means for all 51 samples were 0.19, 21.5, and 0.041 percent. The greater tenor of the heavy minerals and zircon collected from the Coastal Plain of Georgia is pronounced.

Two samples were taken from the Black Mingo formation (lower Eocene) in Berkeley and Georgetown Counties, S. C., and two samples were taken from the McBean formation (middle Eocene) in Calhoun County, S. C. One sample was also taken from the Hawthorne formation (Miocene) in Brantley County, Ga. The tenor in heavy minerals of these 5 samples ranged from 0.02 to 0.28 percent, with a mean value of 0.10 percent; the percentage of zircon ranged from 8 to 24 percent, with a mean value of 17 percent; and the average tenor in zircon of the sands was 0.017 percent. The tenors of these Tertiary formations, taken mainly in South Carolina, are therefore of the same order as those representing the Pleistocene terraces in that State.

The Tuscaloosa formation, of Late Cretaceous age, lies along the southeastern flank of the crystalline rocks. Four collections from McDuffie County, Ga., and one from Johnston County, N. C., show generally higher tenors in heavy minerals and zircon than the Tertiary formations. The Fall Line of the Piedmont province, on which the base of the Tuscaloosa formation rests, is analogous to the higher gradients of bedrock in the headwaters of streams in the monazite belts. Here, more than elsewhere in the Coastal Plain, some gravel may accumulate; and thin beds of coarse and fine gravel are present in the Tuscaloosa. Further concentration by local streams may, with the aid of this gravel, produce local fluvial placers of the heavy minerals. The writer observed in 1951 and recorded (1953, p. 13) such concentrations near Thomson, Ga., and west-northwest of Lexington, S. C. In the following year (1952), a deposit of this kind was located on Horse Creek, a tributary of Savannah River, in Aiken County, S. C.; and later a mining plant was established at this site.

Zircon and other heavy minerals that resist weathering and abrasion may possibly be found in metasedimentary rocks of Precambrian age, with tenors as great as those noted for the Pleistocene sands. This would be true if atmospheric, hydrospheric, and climatic conditions—and the modes of erosion, transportation, and deposition of sediments—were similar to those of today. Similarity of such conditions in early Precambrian time is highly improbable. Yet by some obscure physiographic regimen, some of the Precambrian metasedimentary granitic rocks have tenors in zircon as great as or greater than the mean tenor of the noncommercial Pleistocene sands. Examples will be cited.

## COMMERCIAL DEPOSITS

The mining of detrital deposits of heavy and semiheavy minerals is becoming a worldwide industry, and zircon is commonly one of the minerals recovered from these ores. Commercial deposits of heavy minerals are worked in Brazil, Australia, India, Ceylon, Egypt, the east and west coasts of Africa, the United States, and elsewhere. Australia has been the largest producer of zircon, but the potential production of the United States is probably as great as that of Australia. The principal domestic sources of zircon now being mined are the ilmenite-rutile-zircon placers of Florida, though littoral deposits of heavy minerals also occur at many other sites along the coasts of the Atlantic and Pacific Oceans and the Gulf of Mexico. Some of these will certainly be worked in the near future.

The first deposits of heavy minerals to be mined in Florida were sands, in part dune sands, along the present Atlantic beach. Thus during the World War I, discontinuous deposits of heavy minerals were worked south of St. Johns River in Indian River County, from Mineral City (Ponte Vedra) southward for 17 miles; and similar deposits were also worked in Duval County, north of Mineral City. Discontinuous deposits of heavy minerals were also mined from 1939 to 1943 for 28 miles along the west shore of Indian River, in Brevard and Indian River Counties. In 1952–53, littoral deposits were worked along the Atlantic beach, from 8 to 10 miles south of Melbourne. All these deposits consisted of thin seams of concentrates, of limited length and width. The mining operations were small, and owing to the scattered character of the deposits, the ore-bearing sand, either as mined or partly concentrated, had to be transported by trucks to some centrally located processing plant. One such mill was located at Palm Bay, Brevard County, about 2½ miles south of Melbourne.

Other deposits were soon found inland from the sea. One was about half a mile south of Vero Beach, Indian River County, and about 3 miles from the ocean. Mining began in 1943 and continued for several years. The ore body had a length of about 1,500 feet, a width of about 200 feet, a workable depth of 10–12 feet, and a tenor in heavy minerals of about 5 percent. Zircon constituted about 14 percent of the concentrates. This deposit had a mean altitude of 20–25 feet and therefore was a part of the Pamlico terrace.

A much larger deposit was located about 6 miles east of South Jacksonville, in Duval County, by the Rutile Mining Co., a subsidiary of the Titanium Alloy Manufacturing Co. This property is now owned by the National Lead Co. and is worked by the Humphreys Gold Corporation. The principal part of the deposit lies north of the Atlantic boulevard, a highway that connects South Jacksonville with the Atlantic beaches. Mining began in the principal ore body in 1943 and is now being continued in an extension of the deposit south of the boulevard. From 3,000 to 10,000 tons of sand have been processed daily during the life of this operation—the larger figure applies to the present capacity.

The northern deposit of mineral-bearing sand has a general subelliptic shape, with maximum dimensions of 1 by 4 miles, trending N. 35° E.; but the actual area of 900 acres mined from 1943 to 1956 was indefinite in size and shape, depending upon the tenors found. The depth of the mineral-bearing sand ranged from 12 to 25 feet. When mining began, the tenor in heavy minerals at a minimum depth was about 8 percent; but with the greater depth subsequently mined, the average tenor became about 4 percent. In the final stages of this operation, the tenor may decrease to 3 percent, which is regarded as the lower limit of profitable mining for sands of this mineralogical character. Zircon constitutes about 15 percent of the heavy minerals. The altitude of this deposit ranges from 40 to 65 feet, with a mean altitude of 54 feet. It therefore lies within the Penholoway terrace.

Another deposit in this area that has not yet been mined is about 2½ miles farther south. This has a length of about 3 miles, a width of about half a mile, and a workable thickness of 8–10 feet. The mineral-bearing sand, however, does not begin at the surface, but instead lies at a depth of 20–30 feet. The workable stratum has a tenor in heavy minerals of 4–5 percent, but the overburden is too low grade to be worked at a profit. Therefore a stripping operation will probably be necessary. The altitude at the top of the ore sand is from 25 to 35 feet, and the deposit may therefore be either a part of the Penholoway terrace, or a part of the Talbot terrace buried by Recent dune sand. Mapping of the local shorelines would be necessary in order to decide between these alternatives.

The largest deposit of heavy minerals so far found and worked in Florida is along Trail Ridge, in the western part of Clay County. E. I. du Pont de Nemours Co. owns a large block of ground on this ore body and has established two mining plants, one of which began mining in 1949, the other in 1955. The first plant, about 5 miles east-southeast of Starke, handles about 25,000 tons of ore-bearing sand and overburden daily and doubtless will continue at this rate for many years. Until 1958 the operating company has been the Humphreys Gold Corp., which also has controlled the processing and sale of zircon from this plant. A second plant, called the Highland plant, with about the same capacity, began mining in 1955 on the same paystreak, about 7 miles north of the first plant, and three-quarters of a mile northeast of Lawtey.

The mineral-bearing sand is known to extend for at least 19 miles in a general northerly direction and has a width ranging from 0.5 to 1.5 miles. The ore begins at a depth of 5–10 feet below the surface of the ground, and extends downward from 10 to 65 feet, with an average thickness of about 35 feet. The mean tenor in heavy minerals is about 4 percent. The mineral-bearing sand at the second plant appears to be somewhat thinner than at the first plant, but wider. Zircon is reported to constitute about 13 percent of the concentrates. This deposit occurs at altitudes ranging from 165 to 200 feet and therefore appears to lie dominantly within the Sunderland terrace.

A small deposit of heavy minerals was discovered years ago near Winter Beach, Indian River County, but it was not developed until recently. A mining plant was installed in 1955 by the Florida Minerals Co., a subsidiary of the Hobart Bros. Welding Co., and dredge mining is now in progress. Neither the size nor the tenor of this ore body has yet been fully established, but zircon is reported to constitute 14 percent of the heavy minerals. The paystreak lies in a low ridge that has a maximum altitude of about 40 feet, but the top of the main ore body has an altitude of 10–20 feet. The deposit is probably a part of the Pamlico terrace and has been covered by windblown sand of Recent age.

Considerable prospecting has been done along the Gulf coast of Florida. Stephen H. Rogers, of Tampa, acquired before 1943 an option from the State of Florida to lease the sand deposits along the north shore of Santa Rosa Sound and along three bays east and northeast of Pensacola. These beach deposits were sampled by W. C. Hudson (1943, p. 13–15, 17–18), of the U. S. Bureau of Mines, and were found not to contain a large volume of heavy minerals. In recent years, the Heavy Minerals Co., a subsidiary of the Crane Co., has prospected the beach sands from 15 to 50 miles west of Panama City, particularly in Walton County between Phillips Inlet and Santa Rosa Sound. One sample of the concentrates from these sands showed a tenor of 12 percent in zircon. The weighted average of the tenors in zircon found in the concentrates near Pensacola by Hudson

(1943, p. 13–15, 17–18) was 9.7 percent, but large variations from this mean value were recorded. Little or no prospecting appears to have been done on the higher ground inland from the Gulf of Mexico.

Other deposits of heavy minerals are known in Florida. One of these sites is Amelia Island, along the northeast coast of Florida, at the mouth of St. Marys River, in Nassau County. This island has been extensively prospected by several companies, and one company is now preparing to install a bucket dredge and a separatory plant. The mineral-bearing sand appears to lie within the Pamlico and Silver Bluff terraces. Talbot Island, in Duval County, and Anastasia Island, in St. Johns County, have been prospected by other companies.

The National Lead Co. has acquired a large block of ground in Duval County, north of Highland and east of Macclenny. This appears to be a northern extension of the paystreak of Trail Ridge. Also the Bear Creek Mining Co. has been prospecting in Putnam and Clay Counties, Florida.

Panning by the writer in 1948 (Mertie, 1953, p. 15) in Brantley County, Ga., between Nahunta and Waycross, revealed surficial tenors near Hoboken of about 1 percent of heavy minerals. This suggested that sands of higher grade might lie below the surface and indicated that the paystreak of Trail Ridge might extend northward into Georgia, east of the Okefenokee Swamp. Subsequently, a large block of ground was prospected and acquired by E. I. du Pont de Nemours Co., in Charlton County, Ga. This deposit appears to be on an extension of the paystreak of Trail Ridge, either within the Okefenokee or Sunderland terraces.

Another favorable locality for heavy minerals in Georgia is Cumberland Island, off the east coast of Camden County. This island has been privately owned and used as a winter resort for many years, but recently has been in litigation resulting from the settlement of several estates. Several large companies have cooperated in prospecting on this island, and some of the ore-bearing sands have been found to be minable. Prospecting has also been done on St. Simons Island and inland in the vicinity of Darien.

Considerable prospecting has been done in the northeastern part of North Carolina. Some of this work was done in Chowan, Perquimans, Pasquotank, and Camden Counties, north of Albermarle Sound; some was done between Albermarle Sound and Pamlico River; and some was done in Beaufort and Pamlico Counties, south of the Pamlico River. Options on a part of this ground were taken by one operating company and are still held, though the tenor in heavy minerals is reported to be less than the accepted commercial grade. The deposits appear to be a part of the Pamlico terrace.

No large alluvial deposits of heavy minerals have yet been found in

South Carolina or Virgina, possibly because sufficient prospecting has not been done. Heavy minerals in commercial concentration and volume may be found along any of the Atlantic terraces or beaches, from Florida to New Jersey, and also along the coast of the Gulf of Mexico. A large deposit of heavy minerals has recently been discovered in Ocean and Burlington Counties, N. J., and is now being actively prospected by the American Smelting and Refining Co. and other interested concerns. Ilmenite is reported to be the principal mineral of this deposit, with minor contents of zircon and rutile.

A fluvial deposit of heavy minerals is on Horse Creek, about 13 miles S. 62° W. of Aiken, in Aiken County, S. C. This deposit, owned by the Crane Co., the Vitro Corporation of America, and the Pechiney organization of France, is being dredged by the Heavy Minerals Co., a subsidiary of the Crane Co. The tenor in heavy minerals is about 1½ percent, and the tenor in zircon of the heavy minerals is about 16 percent. Mining is made possible by an unusually high content of monazite and xenotime, which constitute between 10 and 12 percent of the heavy minerals. The ratio of monazite to xenotime is variable but is reported to average 15 : 1.

Zircon occurs in granitic hardrock at a few localities with tenors as great or greater than in some of the littoral deposits, and zircon was mined on a small scale in earlier years from a pegmatite near Zirconia, in Henderson County, N. C. The mean tenor in zircon in 51 noncommercial Pleistocene sands has been shown to be 0.04 percent. Of the hardrock samples hereafter tabulated, 2 have tenors in zircon of 0.08 and 0.12 percent, and 2 have tenors of about 0.03 percent. The zircon grains in these 4 samples are partly or wholly rounded, and the host rocks are believed to be of sedimentary origin. These facts are cited to show that concentrations of heavy minerals are present in some of the metasedimentary granitic rocks of Precambrian age and that these zircons satisfy the first and fourth criteria of heterogeneity heretofore mentioned.

## HAFNIUM-ZIRCONIUM RATIOS

The ratio of hafnium to zirconium in zircon and other minerals is variable. According to Rankama and Sahama (1950, p. 567–568), the mean value of this ratio approaches 0.02. Much higher and much lower rations, however, have been found in special areas and in certain rare minerals. The Hf : Zr ratios in zircon that is taken directly from hardrock have the greatest geological and geochemical interest; ratios obtained from alluvial zircon have superior commercial value.

Zircon has many uses in which the presence of large or small percentages of hafnium are immaterial; but for some purposes, either a very high or a very low tenor is hafnium is desired. It is impracticable to separate two such varieties from alluvial deposits. If it is required to learn the range of the tenor in hafnium, either for scientific or economic reasons, it is necessary to obtain zircon directly from bedrock sources. It has been shown, however, that zircon taken directly from bedrock is not necessarily homogeneous; yet such samples are superior in this regard to alluvial samples because heterogeneity, if present, is less pronounced. Thus, heterogeneous samples of zircon from bedrock were derived from different source rocks, but these sources probably were genetically related and were not far separated geographically. On the other hand, heterogeneous samples of zircon from the Atlantic beaches represent scores or even hundreds of source rocks of many different types from widely separated areas.

## EARLIER DETERMINATIONS

The Hf : Zr ratios of 113 samples of zircon, and 32 varieties thereof, have been compiled by Michael Fleischer (1955, p. 5–7). The original publications for most of these samples did not state their exact localities; but most of the samples are believed to represent alluvial zircon, though some were doubtless taken directly from bedrock. The mean values of the Hf : Zr ratios for 40 samples of zircon from this group is 0.027, with maximum and minimum values respectively of 0.100 and 0.002.

Tugarinov, Vaynshteyn, and Shevaleyevsky (1956, p. 31) have recently published the percentages of $ZrO_2$ and $HfO_2$ in 31 samples of zircon and malacon, taken from migmatitic gneisses, granites, pegmatities, syenites, and metasomatic deposits in the Ukrainian S. S. R. Recomputed to Hf : Zr ratios, the mean value is found to be 0.028, with maximum and minimum values of 0.072 and 0.011. Lipova, Shevaleyevsky, and Tuzova (1957, p. 139) have published the tenors in zirconium and hafnium of 9 samples of zircon from the granitic rocks of the Verkhissetsk area, U. S. S. R. Computed to Hf : Zr ratios, the mean value is found to be 0.023, with maximum and minimum values of 0.029 and 0.014. Pavlenko, Vaynshteyn, and Shevaleyevsky (1957, p. 351–367) have published the percentages of $ZrO_2$ and $HfO_2$ in 47 samples of vein rocks and metasomatic rocks from eastern Tuva, U. S. S. R. Reduced to Hf : Zr ratios, the mean value is found to be 0.025, with maximum and minimum values of 0.082 and 0.005. And Gerasimovsky and Shevaleyevsky (1957, p. 696–698) have published the percentages of $ZrO_2$ and $HfO_2$ in 36 samples of zircon, eudialyte, lovozerite, catapleiite, lavenite, zirfesite, and belyankinite from the Kola Peninsula, northern Russia. Only 7 of these samples are zircon, with a mean Hf : Zr ratio of 0.023. The maximum, minimum, and mean Hf : Zr ratios for the 36 samples are respectively 0.031, 0.015, and 0.021.

## PRESENT INVESTIGATION

A study of the granitic rocks of the Southeastern Atlantic States has been conducted for 10 years by the U. S. Geological Survey, and in this work the writer has collected 700 samples of accessory minerals from 134 counties of 6 States. Thirty samples of zircon from these collections were selected for determinations of their Hf : Zr ratios; and for comparison, 3 samples of alluvial zircon from Florida and 6 from foreign countries were also analyzed. The percentages of zircon in the accessory minerals, and the tenors in zircon of these granitic rocks, were also determined.

The zircon from bedrock was obtained by panning large samples (100–500 pounds) of granitic saprolite, from which sizable samples of accessory minerals were recovered. These, and also the alluvial concentrates, were separated magnetically into four fractions, of which one was nonmagnetic. These nonmagnetic fractions consisted mainly of quartz and zircon, as samples containing rutile were not used. Samples completely free of quartz and other minerals, however, were needed for the spectroscopic work. Such samples were obtained by dividing small parts of the nonmagnetic fractions into mineralogical subfractions by more refined electromagnetic separation and by immersion in heavy solutions. The presence of unwanted nonmagnetic minerals in some of the alluvial samples necessitated handpicking under a binocular microscope. This final purification was done in the laboratory of the U. S. Geological Survey by David Gottfried and William F. Outerbridge.

The tenors in zircon of the concentrates recovered from bedrock were determined by weighing the nonmagnetic fractions and by estimating the percentages of zircon in them. The tenors in zircon of bedrock were determined by comparing the weights of zircon recovered from the nonmagnetic fractions with the weights of the corresponding samples of saprolite. The principal errors in these two percentages of zircon result from losses in panning, inaccuracy in estimating the tenors in zircon of the nonmagnetic fractions, and inaccuracy in gauging the weights of the saprolitic samples. A skilled panner can rarely recover more than 80–90 percent of minerals having specific gravities of 3.5–5. Losses in zircon, however, are less than the average, because the small grains of zircon from granite tend to remain at the bottom of a gold pan, covered by larger and more abundant grains of iron ores and other accessory minerals. A moderately heaped pan of saprolite is assigned arbitrarily a weight of 10 kilograms (22 lb); and considering variations in moisture, compaction, and other variables, this is an acceptable average weight. Inaccuracies in the estimation of zircon in the concentrates, and in gaging the weights of the samples of saprolite, are believed to be less than those incurred in panning.

### LOCALITIES OF SAMPLES

The following list presents the localities of 30 samples of zircon taken from bedrock. Three samples of alluvial zircon, whose localities are also given, came from mining plants in Florida. Six other alluvial samples included 1 from Brazil, 2 from Australia, 1 from Egypt, 1 from the Panamanian Canal Zone, and 1 from Ceylon. The sample from Brazil was contributed by William D. Johnston, Jr., of the U. S. Geological Survey; the sample from Queensland was furnished by J. H. Morley, of the American Rutile Corp., formerly at Roseland, Va.; and the other 4 were donated by J. Hall Carpenter, president of Carpco Manufacturing, Inc., and affiliated companies, of Jacksonville, Fla.

*Localities of bedrock samples*

**Virginia**

| *Field sample* | |
|---|---|
| 50 Mt 188 | Saprolite of granitic gneiss from Wissahickon formation. Locality, southwest side of Route 969, and 16.5 miles airline S. 61° E. of Rocky Mount, Franklin County, Va. |
| 50 Mt 201 | Saprolite of Grayson granodiorite gneiss. Locality, north side of Route 58, and 5.9 miles airline S. 88° W. of Independence, Grayson County, Va. |
| 50 Mt 234 | Saprolite of monazite-bearing granitized gneiss of the Wissahickon formation. Locality, east side of Route 58, 200 yards north of Nottoway River, and 6.2 miles airline S. 20° E. of Blackstone, Nottoway County, Va. |
| 54 Mt 60 | Saprolite of monazite-bearing phase of Petersburg granite. Locality, south side Route 360, and 6.0 miles airline N. 36° W. of Chesterfield, Chesterfield County, Va. |
| 54 Mt 90 | Saprolite of Lovingston granite gneiss. Locality, east side of Route 56, and 2.2 miles airline N. 11° E. of Lovingston, Nelson County, Va. |
| 55 Mt 23 | Saprolite of Marshall granite. Locality, east side of Route 637, one-third mile north of bridge over Jordan River, and 3.6 miles airline N. 89° E. of Flint Hill, Rappahannock County, Va. |
| 55 Mt 45 | Saprolite of monazite-bearing migmatitic gneiss in Catoctin greenstone. Location, south side of Route 55, and three-quarters mile east of Markham, Fauquier County, Va. |
| 55 Mt 49 | Saprolite of hypersthene granodiorite (Pedlar formation of Bloomer and Werner, 1955). Northeast side of Route 33, and 2.7 miles airline N. 54° W. of Stanardsville, Greene County, Va. |

**North Carolina**

| | |
|---|---|
| 45 Mt 118 | Saprolite of granite near Gastonia. Locality, north side of Route 74, and 2.1 miles airline S. $86^{1}/_{2}$° W. of center of Gastonia, Gaston County, N. C. |
| 47 Mt 12 | Saprolite of pegmatite at old Zirconia mine. Locality, southeast side Route 25, and 6.7 miles airline S. 17° E. of Hendersonville, Henderson County, N. C. |

*Localities of bedrock somples*—Continued

**North Carolina—Continued**

| *Field sample* | |
|---|---|
| 47 Mt 17 | Saprolite of Henderson granite. Locality, top of Balfour quarry on northwest side, and 3.5 miles airline N. 15° W. of Hendersonville, Henderson County, N. C. |
| 47 Mt 23 | Milled sample of Beech granite. Locality, east side of unpaved road, and 1.3 miles airline N. 34° E. of Heaton, Avery County, N. C. |
| 47 Mt 47–a | Saprolite of Carolina gneiss. Locality, north side of Route 19–23, and 2.3 miles airline N. 78° E. of Luther, Buncombe County, N. C. |
| 47 Mt 71 | Saprolite of monazite-bearing Toluca quartz monzonite. Locality, west side of Route 18, about 2.5 miles by road north-northwest of Jacob Fork River, and 3.0 miles airline N. 21° W. of Ramsey, Burke County, N. C. |
| 47 Mt 75 | Residual pegmatitic zircon from ploughed field. Locality, east side of unpaved road, about one-half mile north-northwest of Max's Service Station at Loray, Iredell County, N. C. |
| 48 Mt 22 | Saprolite of zircon-rich phase of Roan gneiss. Locality, west side of Route 19–E, and 1.1 miles airline N. 9° E. of Minneapolis, Avery County, N. C. |
| 48 Mt 39 | Saprolite of Blowing Rock gneiss. Locality, northeast side of Route 321, and 2.3 miles airline S. 40° E. of Blowing Rock, in Caldwell County, N. C. |
| 49 Mt 119 | Saprolite of quartz-bearing syenite. Locality, mining pit west of Route 29, and 3.5 miles airline S. 20° W. of Concord, Cabarrus County, N. C. |
| 50 Mt 164 | Saprolite of monazite-bearing coarse-grained porphyritic granite. Locality, south side of Route 74, and 3.2 miles airline S. 78° E. of Wadesboro, Anson County, N. C. |

**South Carolina**

| | |
|---|---|
| 47 Mt 37 | Saprolite of granite gneiss adjacent to pegmatite at vermiculite mine. Locality, south side of Route 43, and 0.5 mile N. 70° E. of Tigerville, Greenville County, S. C. |
| 48 Mt 18 | Saprolite of granite. Locality, southeast side of Route 105, and 4.7 miles S. 26° E. of Wilkinsville, Cherokee County, S. C. |
| 51 Mt 105 | Saprolite of monazite-bearing granite. Locality, north side of paved road, just west of Rockton-Rion railroad, and 5.4 miles airline S. 22° W. of Winnsboro, Fairfield County, S. C. |
| 55 Mt 38 | Saprolite of granite. Locality, north side Route 601 (State route 9), 200 yards east of Lynches River, and 5.7 miles airline N. 56° W. of Jefferson, Chesterfield County, S. C. |

### *Localities of bedrock samples*—Continued

#### Georgia

| *Field sample* | |
|---|---|
| 45 Mt 26 | Saprolite of Lithonia granite gneiss (as used by Herrmann, 1954). Locality, north side of entrance to Rock Chapel quarry, and 3.6 miles airline N. 34° E. of Lithonia, De Kalb County, Ga. |
| 50 Mt 68 | Saprolite of monazite-bearing granite. Locality, atop and at southeast end of Tyrone quarry, on east side of Route 74, and 0.6 mile airline south of Tyrone, Fayette County, Ga. |
| 50 Mt 70 | Saprolite of monazite-bearing granite gneiss. Locality, southeast side of Route 14, and 3.3 miles S. 68° W. of La Grange, Troup County, Ga. |
| 50 Mt 90 | Saprolite of granite. Locality, east side of Route 154, and 3.2 miles N. 36° W. of Palmetto, Fulton County, Ga. |
| 50 Mt 106 | Saprolite of monazite-bearing gneissoid granite. Locality, northwest side of unpaved road, and 4.2 miles airline S. 32° E. of Clermont, Hall County, Ga. |
| 51 Mt 27 | Saprolite of granite gneiss. Locality, north entrance to Camak quarry, on northwest side unpaved road, and 4.2 miles airline N. 26° E. of Camak, Warren County, Ga. |

#### Tennessee

| | |
|---|---|
| 47 Mt 32 | Saprolite of Max Patch granite. Locality, east side of unpaved road connecting Del Rio, Tenn., with Crabtree N. C., and 0.3 mile north of Lemon Pass, Cocke County, Tenn. |

### *Localities of alluvial samples*

#### Florida

| *Field sample* | |
|---|---|
| 45 Mt 49 | Zircon from plant of Riz Mineral Co., about half a mile south of Vero Beach, Indian River County, Fla. |
| 50 Mt 8 | Zircon from plant of E. I. du Pont Nemours Co., about 5 miles S. 63° E. of Starke, Clay County, Fla. |
| 50 Mt 11 | Zircon from plant of National Lead Co., about 6 miles east of South Jacksonville, Duval County, Fla. |

#### Foreign Countries

| | |
|---|---|
| 51 Mt 248 | Zircon separated from heavy minerals recovered from delta of Nile River, Egypt. |
| 51 Mt 254 | Zircon separated from heavy minerals recovered from beach at Guarapari, Espirito Santo, Brazil. |
| 53 Mt 128 | Zircon separated from heavy minerals recovered from beach at Colon, Panamanian Canal Zone. |
| 54 Mt 146 | Zircon separated from heavy minerals recovered from beach at North Stradbroke Island, Queensland, Australia. |
| 55 Mt 13 | Zircon separated from heavy minerals recovered from beach at Cudgen Headland, New South Wales, about 80 miles south of Brisbane, Australia. |
| 55 Mt 10 | Zircon separated from heavy minerals recovered on Pulmaudi Beach, northeastern Ceylon. |

## MINERALOGIC AND SPECTROSCOPIC DATA

The percentages of zircon in the concentrates recovered from 30 samples taken from bedrock, the percentages of zircon in the corresponding samples of saprolite, and the Hf:Zr ratios of the zircons are presented in table 1. The Hf:Zr ratios of the zircon taken from nine alluvial samples are shown in table 2.

These ratios were determined independently by spectrographic analysis and by the method of X-ray fluorescence. This work was done in the laboratory of the U. S. Geological Survey by Claude L. Waring, Helen W. Worthing, and Isidore Adler.

TABLE 1.—*Zircon in bedrock*

| Field sample | Percent in concentrates | Percent in bedrock | Hf: Zr ratio | |
|---|---|---|---|---|
| | | | Spectrographic | X-ray fluorescence |
| **Virginia** | | | | |
| 50 Mt 188 | 80 | 0.0058 | 0.023 | 0.022 |
| 50 Mt 201 | 3 | .0087 | .022 | .022 |
| 50 Mt 234[1] | 33 | .0060 | .026 | .027 |
| 54 Mt 60[1] | 0.1 | .00005 | .025 | .026 |
| 54 Mt 90 | 99.9 | .081 | .021 | .020 |
| 55 Mt 23 | 75 | .032 | .022 | .026 |
| 55 Mt 45[1] | 12 | .011 | .027 | .026 |
| 55 Mt 49 | 89 | .026 | .021 | .021 |
| **North Carolina** | | | | |
| 45 Mt 118 | 61.7 | 0.0020 | 0.020 | 0.022 |
| 47 Mt 12 | [2] ND | ND | .017 | .018 |
| 47 Mt 17 | 2.8 | .00034 | .028 | .028 |
| 47 Mt 23 | 4 | .00081 | .035 | .030 |
| 47 Mt 47-a | 4.7 | .0098 | .022 | .022 |
| 47 Mt 71[1] | 3.2 | .00023 | .034 | .030 |
| 47 Mt 75 | ND | ND | .018 | .015 |
| 48 Mt 22 | 90 | .0090 | .026 | .022 |
| 48 Mt 39 | 80 | .023 | .028 | .025 |
| 49 Mt 119 | 5 | .12 | .018 | .016 |
| 50 Mt 164[1] | .7 | .0025 | .025 | .024 |
| **South Carolina** | | | | |
| 47 Mt 37 | ND | ND | 0.021 | 0.018 |
| 48 Mt 18 | 0.7 | 0.011 | .025 | .024 |
| 51 Mt 105[1] | .1 | .00013 | .027 | .027 |
| 55 Mt 38 | 2 | .0093 | .024 | .024 |
| **Georgia** | | | | |
| 45 Mt 26 | 2 | 0.00072 | 0.028 | 0.028 |
| 50 Mt 68[1] | 2 | .0034 | .029 | .028 |
| 50 Mt 70[1] | 1.4 | .0075 | .025 | .031 |
| 50 Mt 90 | 7 | .0035 | .022 | .024 |
| 50 Mt 106[1] | 1.8 | .011 | .028 | .027 |
| 51 Mt 27 | 4 | .0083 | .025 | .024 |
| **Tennessee** | | | | |
| 47 Mt 32 | 57.9 | 0.0092 | 0.022 | 0.024 |

[1] Monazite-bearing.
[2] Not determined.

TABLE 2.—*Alluvial zircon*

| Field sample | Hf:Zr ratios | |
|---|---|---|
| | Spectrographic | X-ray fluorescence |
| **Florida** | | |
| 45 Mt 49 | 0.024 | 0.023 |
| Duplicate | .022 | .023 |
| 50 Mt 8 | .022 | .023 |
| Duplicate | .021 | .022 |
| 50 Mt 11 | .022 | .027 |
| Duplicate | .022 | .025 |
| Triplicate | ---------- | .025 |
| **Foreign Countries** | | |
| 51 Mt 248 | 0.022 | 0.024 |
| Duplicate | .021 | .022 |
| 51 Mt 254 | .026 | .029 |
| Duplicate | .023 | .030 |
| 53 Mt 128 | .022 | .025 |
| Duplicate | .022 | .025 |
| 54 Mt 146 | .023 | .025 |
| Duplicate | .024 | .025 |
| 55 Mt 13 | .024 | .025 |
| Duplicate | .026 | .026 |
| 55 Mt 10 | .024 | .023 |
| Duplicate | .026 | .023 |

## APPRAISAL OF HF:ZR RATIOS

The tenor in zirconium increases generally from the ultramafic and mafic rocks to the most siliceous of the granitic rocks. The ratio of hafnium to zirconium, however, is low in the granitic rocks and is erratic in other rocks. The preceding analyses were made to show the variations of the Hf:Zr ratio in the granitic rocks of the Southeastern Atlantic States and to locate, if possible, any zircon that might have a very low or an unusually high tenor in hafnium. But no very low or very high ratios were found, either in the zircon taken from bedrock or in the alluvial zircon of Florida. Certain other relationships, however, were deduced.

Complete quantitative data on the tenors in zircon of all the granitic rocks of the Southeastern States, and also on the tenors in hafnium of zircon, will not be available until the crystalline rocks of this region are systematically studied and mapped. The results shown in the preceding table may not be generally representative of the granitic rocks, because the samples were taken from saprolites that yielded either a large volume of concentrates containing little zircon, or a smaller volume of concentrates that were dominantly zircon. This selection was rendered necessary for economic reasons, as obviously the presence of zircon high or low in hafnium is not commercially important unless the amounts obtainable are significant. A few exceptions to this mode of selection were made—notably samples 54 Mt 60 and 47 Mt 71, which were included for other reasons.

The values of the Hf:Zr ratios in table 1, measured by the methods of spectrography and X-ray fluorescence, are generally comparable in their orders of magnitude. Seven determinations are identical by the 2 methods; 15 are greater by the method of spectrography; and 8 are greater by the method of X-ray fluorescence. Eleven differ by 0.001, 4 by 0.002, 3 by 0.003, 3 by 0.004, 1 by 0.005, and 1 by 0.006. The mean difference for the 30 determinations, neglecting algebraic sign, is therefore 0.0017. The mean values of the Hf:Zr ratios by the 2 methods are nearly identical; that is, respectively, 0.0245 and 0.0240; and the general mean is thus 0.0242. More consistent results could not be demanded.

A comparison of the monazite-bearing samples with those that contain no monazite appears to have some significance. To make this comparison, a third group, consisting of 3 samples of pegmatitic origin and 1 of a quartz-bearing syenite, was eliminated, as these 4 samples are not representative of ordinary granites and gneisses. The third group comprises samples 47 Mt 12, 47 Mt 75, 47 Mt 37, and 49 Mt 119. The first, or monazite-bearing group, includes 9 samples; the second group, containing no monazite, includes 17 samples. No low values of the Hf:Zr ratio occur in group 1, and the mean values by the 2 methods of analysis are identical—0.0273. The corresponding mean values for group 2 are 0.0244 and 0.0240, with a general mean of 0.0242. The zircon of group 3, however, has a mean Hf:Zr ratio of only 0.0176.

Deductions or inferences based upon such a small number of samples are necessarily subject to considerable doubt. It appears, however, that the difference of 0.0031 in the mean ratios of groups 1 and 2 is too large to be accidental. No reason can be suggested why the Hf:Zr ratios of monazite-bearing rocks should be greater than for rocks that contain no monazite, but this anomaly deserves at least to be recorded. The Hf:Zr ratios of the 3 pegmatites and the quartz syenite are individually lower than the mean ratios of either group 1 or 2, and their mean ratio is 0.0077 less than the mean ratio for the other 26 samples.

The samples of groups 1 and 2 were then divided into 4 subgroups based upon genetic relationships. These 4 fractions included 12 samples of paragneiss, 4 samples of metasedimentary rocks, 4 samples of magmatic rocks, and 6 samples of rocks of undetermined origin. Another quadripartition of the 17 samples of non-monazite-bearing rocks that comprise group 2 was also made on the same genetic basis. None of the 8 resulting groups of ratios appears to be sufficiently distinctive to indicate any significant relationships. These results suggest that all the granitic rocks selected for this analysis, even those listed as magmatic in origin, contained either heterogeneous zircon, or magmatic zircon remelted from sedimentary or metasedimentary rocks. Thus, mixing of the zircons may already have been far advanced in late Precambrian time. This conclusion, if verified by further investigation, should deter geologists from submitting samples of zircon from Precambrian metasedimentary rocks for radiometric age determinations.

The mean value of 13 determinations of the Hf:Zr ratios in samples from Florida is 0.023. This is appreciably less than the value of 0.027, determined by Cooley and others (1953, p. 31), and is more in agreement with the mean value of 0.024, for 30 determinations of zircon from bedrock in the Southeastern States. These 4 authors also published 12 other spectrographic determinations of Hf:Zr ratios, all of which were included by Fleischer (1955) in his compilation. Two of these samples came from Coos Bay, Oregon, 2 from India, 3 from Australia, 3 from Brazil, 1 from North Carolina, and 1 from Berks County, southeastern Pennsylvania. Excepting Coos Bay, no exact localities were given, but all the samples are believed to represent alluvial zircon.

The mean value of the Hf:Zr ratios given by Cooley and collaborators for the samples from Australia and Brazil are, respectively, 0.017 and 0.011, whereas those shown in the table 2 for these 2 countries are, respectively, 0.025 and 0.027. Discrepancies of this order could be caused either by collecting at widely separated localities, by imperfect purification of the samples, or by errors arising from analytical procedures in the laboratory. But the ratios of alluvial zircon in any one general locality tend to approach a constant mean value. Yet 1 of the ratios by Cooley and collaborators for a sample from Queensland is 0.015, whereas 1 sample from Queensland, included in table 2, shows a mean value of 0.024. Probably both these samples came from the great deposit of heavy minerals on Stradbroke Island, and it is improbable that any such difference exists within this general area. The difference in these ratios may therefore result either from improper preparation of the sample or from dissimilarity in the techniques used in the laboratory.

## PRODUCTION, IMPORTS, AND RESERVES

The domestic production and imports of zircon in recent years are shown in the following table. The sources of these figures are data published in the Minerals Yearbooks of the U. S. Bureau of Mines, particularly in the papers by Griffith (1956, p. 1321) and Reno (1958, p. 1–8), and unpublished data supplied by the same organization; Australia is the principal source of imported zircon.

*Domestic production and imports of zircon (short tons), 1950–56*

| *Year* | *Production* | *Imports* |
|---|---|---|
| 1950 | | 16, 129 |
| 1951 | | 25, 208 |
| 1952 | | 21, 935 |
| 1953 | 23, 900 | 23, 461 |
| 1954 | 16, 300 | 17, 249 |
| 1955 | 28, 110 | 29, 091 |
| 1956 | 43, 980 | 31, 140 |

The volume of heavy minerals, including zircon, that exist in all the sands of the Coastal Plain is enormous. Zircon appears to be universally present; and it may be assumed, on the basis of the panning mentioned before, that the Cretaceous, Tertiary, and Quaternary formations include billions of tons of sands that have a minimum tenor in heavy minerals of about 0.02 percent. The corresponding tenor in zircon of these sands may be 0.004 percent. Most of these minerals, however, are not recoverable.

Large mining concerns wish to have in sight at least 50 million tons of ore-bearing sand with a proved tenor of not less than 4 percent in heavy minerals before establishing a mining plant. In the latter stages of such mining, when all equipment has been amortized, ore with a tenor of 3 percent, or even less, may be mined. An operation of this magnitude, with a daily treatment of 10,000 tons of ore, should have a life of 15 years and should yield a total production of 250,000 tons of zircon. This estimate takes into account a diminishing tenor in heavy minerals in the late stages of mining and losses in processing.

The reserves cannot be measured accurately, but a rough estimate can be made with a general knowledge of the activities of the companies now operating or preparing to operate, the tenor of ground already prospected, and the areas that are sufficiently good to be held for possible future development. A conservative appraisal of the reserves of zircon contained in minable deposits of heavy minerals in the Southeastern States is 10,000,000 short tons; and the corresponding amounts of zirconium and hafnium, using the mean ratio Hf:Zr= 0.023, are approximately 4,868,000 and 112,000 tons. Based upon plants now in operation and those scheduled soon to come into production, about 100,000 tons of zircon could be produced annually in Florida if needed. The latest available figures on the domestic output, however, show less than half this amount. It therefore is inferred that a considerable volume of zircon-bearing tailings, which remain after the removal of ilmenite, leucoxene, and rutile, are stockpiled for future processing. This may result from conditions of the market, or for other reasons.

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