

# ZIRCON: A REVIEW, WITH EMPHASIS ON WEST COAST RESOURCES AND MARKETS

By A. J. Kauffman, Jr., and Dean C. Holt

\* \* \* \* \* information circular 8268



UNITED STATES DEPARTMENT OF THE INTERIOR  
BUREAU OF MINES

This publication has been cataloged as follows:

**Kauffman, Albert J**

Zircon: a review, with emphasis on west coast resources and markets, by A. J. Kauffman, Jr. and Dean C. Holt. [Washington] U.S. Dept. of the Interior, Bureau of Mines [1965]

69 p. illus., tables. (U. S. Bureau of Mines. Information circular 8268)

Includes bibliography.

1. Zircon. I. Holt, Dean C., jt. auth. (Series)

TN23.U71 no. 8268 622.06173

U. S. Dept. of the Int. Library

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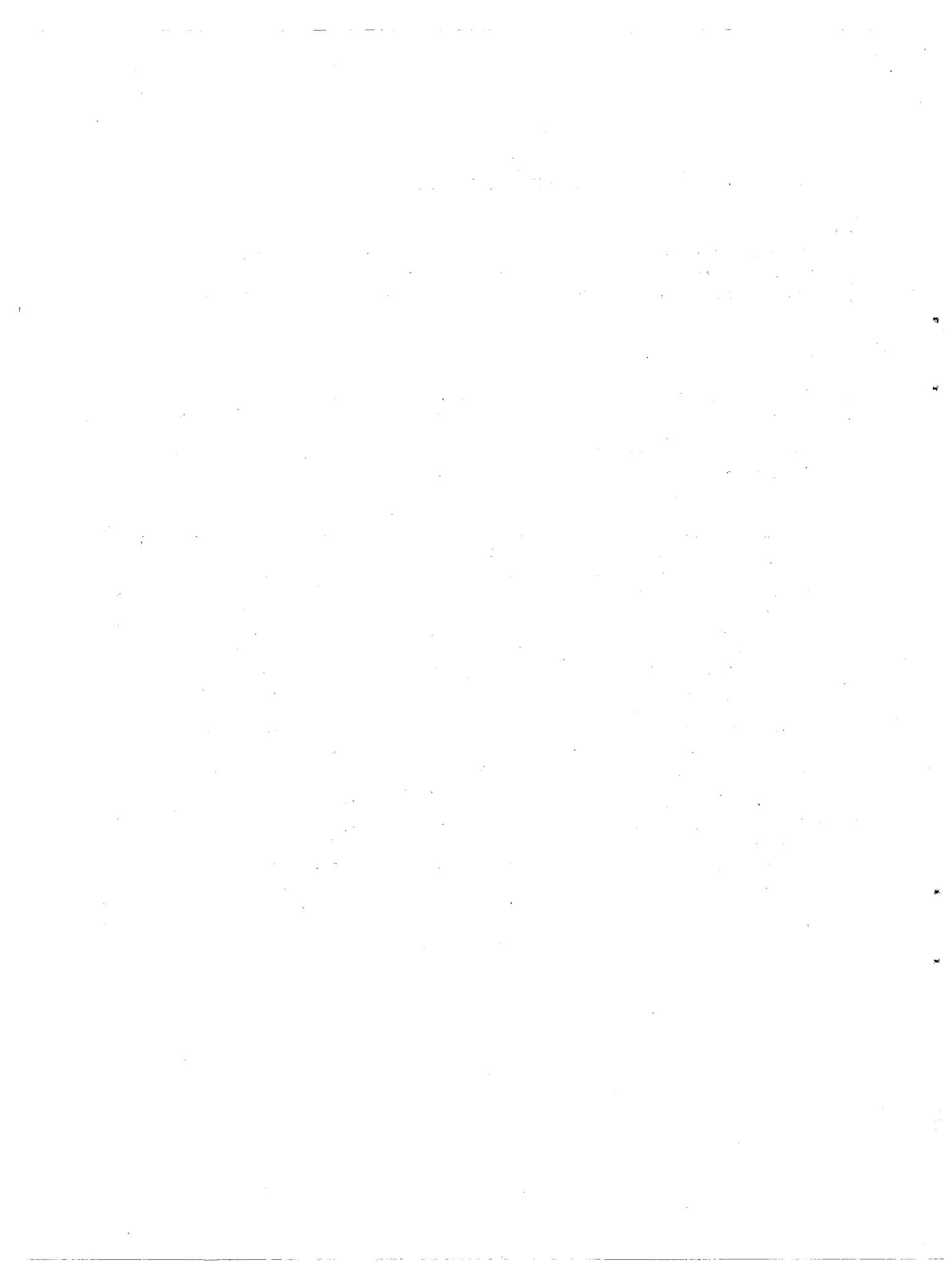
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by

A. J. Kauffman, Jr.<sup>1</sup> and Dean C. Holt<sup>2</sup>

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## ABSTRACT

This study compiles data on the zircon resources of the Pacific Northwest States, Alaska, and California, to determine the productive capability of industrial concerns to make ductile zirconium and hafnium, and to investigate markets for the nonmetallic products of zircon.

West coast zircon resources are large but mostly marginal to submarginal. Development of a stable and profitable zircon mining industry on the west coast will depend upon recovery and utilization of the other associated heavy minerals needed by regional and national markets.

The west coast has the only completely integrated facility for processing zircon sand to reactor-grade zirconium and hafnium and for making fabricated products from these metals. The future of the zirconium metal industry appears to be good because of increased use of the metal for nuclear propulsion and power-generating plants.

## INTRODUCTION

This comprehensive study of zircon appraises the resource and market potential of the Pacific Northwest States, Alaska, and California, and the position of zircon's related industries in the United States is analyzed.

Evaluation of west coast zircon resources is an important first step in assessing the future potential of the commodity in the area. The Bureau of Mines, under sponsorship of the Atomic Energy Commission, undertook an extensive program of exploration and reconnaissance to evaluate deposits of

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alluvial materials. The program, initiated in 1948 and completed in 1955, was directed primarily at locating minable concentrations of monazite and radioactive black minerals. Data gathered on zircon, one of the associated minerals, were used freely in the resource section of this report. Field samples were sent to the laboratory where screen analyses were usually made of both the original gravels and the composited concentrates. A visual and radiometric estimate of mineral content was made for each concentrate fraction. The percentages of ilmenite, monazite, zircon, and other minerals were determined by grain count. No attempt was made to evaluate any of the placers for their gold content.

Alluvial deposits within the area under consideration have been investigated and worked with varying degrees of intensity since about the middle of the 19th century. Early efforts were centered about the gold content of the placers. More recently, interest has been focused on the associated heavy mineral constituents. Oregon beach sands have been exploited for their chromite, and Idaho stream placers have been dredged for monazite and radioactive blacks. To date, virtually no zircon has entered the industrial complex from these sources.

#### SOURCES OF ZIRCONIUM MINERALS

Until recent years, zirconium was considered to be a rare element, even though the earth's crust contains 0.02 to 0.03 percent of the metal. Actually, it is more plentiful than nickel, copper, lead, zinc, and some of the other familiar metals. Zircon, an orthosilicate with the formula  $ZrSiO_4$  (theoretically 67.2 percent  $ZrO_2$  and 32.8 percent  $SiO_2$ ), is the most widely distributed and most important source of the metal. Baddeleyite, an oxide of zirconium,  $(ZrO_2)$ , is a less important source mineral because of its restricted occurrence.

Zircon is a common constituent of many rocks, particularly granites, syenites, and diorites, and of sands resulting from the disintegration of these rocks. It occurs as crystals and as grains. Sedimentary rocks often contain zircon because the mineral is hard and resistant to weathering. It occurs more rarely in granular limestones, schists, and gneisses.

Potential commercial concentrations of zircon are restricted almost entirely to beach-sand and stream-placer deposits; however, titaniferous sandstone deposits in Montana contain a potentially recoverable quantity of zircon. These sandstone deposits resemble, in many ways, our present day beach-sand deposits. Because many of the minerals associated with zircon in alluvial deposits are dark in color, such occurrences are often referred to as "black-sand" deposits.

Baddeleyite occurs as rounded pebbles sometimes called "favas de zirconio." In the trade, the term "baddeleyite" refers to the variety that occurs as distinct crystals, and the term "brazilite" applies to the fibrous, botryoidal or columnar form. The trade name "Zirkite"<sup>3</sup> denotes a mixture of baddeleyite or brazilite and zircon.

<sup>3</sup> Reference to specific brands is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

atomic number 72

Hf  
 Hafnium and zirconium are always associated together, and with the exception of the rare mineral thortveitite, zirconium always predominates. The hafnia content of zircon and baddeleyite generally ranges between 1.0 to 2.0 percent and 1.0 to 1.2 percent, respectively. A treatise on the hafnium content of domestic and foreign zirconium minerals gives more detailed information. (21).<sup>4</sup>

Certain ill-defined, altered varieties of zircon that have not been found in commercial quantities range from 1.7 to 15.0 percent hafnia.

Some interest has been shown recently in zircon from Nigeria containing as much as 4.5 percent hafnium oxide; however, processing the material is attended with metallurgical problems that have not been completely resolved. As a result, it is not being used as a high-hafnium source at present.

Most of the world's supply of zircon has come from Australia where it has been recovered as a coproduct with rutile, ilmenite, and monazite. For a while Australia exported a product containing all four of these minerals. The Australian Government prohibited export of monazite after March 1948. Mixtures of zircon, rutile, and ilmenite continued to be exported to the United States until 1954. Thereafter, essentially all exports of zircon have been shipped as high-grade zircon concentrates.

In Brazil, zircon is found in the States of Bahia, Espirito Santo, and Rio de Janeiro; baddeleyite occurs in the Poços de Caldas region of the States of Minas Gerais and Sao Paulo.

Zircon in India is associated with ilmenite, rutile, and monazite in the beach-sand deposits of Travancore. Rich occurrences of zircon in black sands also are known near Trincomalee on the east coast of Ceylon, and commercial production has been reported from the Republic of Senegal, Malaysia, Republic of South Africa, Malagasy Republic, Nigeria, and the United Arab Republic.

In addition to zircon occurrences in Idaho, Montana, Oregon, Washington, California, and Alaska, the mineral also occurs abundantly in Florida, South Carolina, and Georgia. Zircon, or its altered varieties, also has been found in Arkansas, Arizona, Colorado, Connecticut, Maine, Massachusetts, Mississippi, New Jersey, North Carolina, Pennsylvania, Texas, Virginia, and Wyoming.

Free World production of zircon is found in table 1.

## INDUSTRY

### Mining

Currently all of the domestic production of zircon is in Florida, where a thriving ilmenite mining industry makes it feasible to recover zircon as a coproduct. Increased output of ilmenite and rutile has led to record zircon production.

<sup>4</sup> Underlined numbers in parentheses refer to items listed in the references at the end of this report.

TABLE 1. - Free World production of zircon,  
1948-63  
 (Tons)

Year	Australia	Brazil <sup>1</sup>	United Arab Republic (Egypt)	Republic of Senegal (French West Africa)	Malagasy Republic (Madagascar)	Federation of Malaya	United States	India	Nigeria	Republic of South Africa
1948	25,017	<sup>2</sup> 4,011	104	211	-	-	( <sup>3</sup> )	( <sup>4</sup> )	-	-
1949	23,156	<sup>2</sup> 2,977	141	270	-	-	( <sup>3</sup> )	( <sup>4</sup> )	-	-
1950	24,120	3,325	105	243	-	-	( <sup>3</sup> )	( <sup>4</sup> )	-	-
1951	47,006	3,854	4	32	-	-	( <sup>3</sup> )	( <sup>4</sup> )	-	-
1952	32,893	4,378	133	-	5	-	( <sup>3</sup> )	( <sup>4</sup> )	-	-
1953	30,081	3,409	263	1,047	-	-	23,904	( <sup>4</sup> )	-	-
1954	45,830	4,173	109	1,012	-	-	16,322	( <sup>4</sup> )	-	-
1955	53,994	3,312	126	-	-	-	28,110	( <sup>4</sup> )	-	-
1956	80,382	<sup>5</sup> 1,000	402	1,268	-	51	43,980	( <sup>4</sup> )	-	-
1957	99,188	1,799	45	3,197	1	<sup>2</sup> 47	56,802	10	101	-
1958	66,381	10,471	<sup>5</sup> 45	7,606	58	<sup>2</sup> 28	30,443	10	-	1,129
1959	125,834	10,846	<sup>5</sup> 65	9,557	50	130	( <sup>3</sup> )	<sup>5</sup> 10	1,250	5,924
1960	114,645	6,358	408	11,408	145	63	( <sup>3</sup> )	<sup>5</sup> 10	1,968	7,366
1961	152,859	7,405	( <sup>4</sup> )	5,939	353	<sup>2</sup> 63	( <sup>3</sup> )	<sup>5</sup> 10	832	7,607
1962	149,869	2,642	188	2,575	390	<sup>2</sup> 67	( <sup>3</sup> )	( <sup>4</sup> )	<sup>6</sup> 544	7,581
1963	<sup>5</sup> 185,000	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>3</sup> )	( <sup>4</sup> )	886	<sup>5</sup> 3,500

<sup>1</sup> Mainly baddeleyite.

<sup>2</sup> Exports.

<sup>3</sup> Figure withheld to avoid disclosing individual company confidential data.

<sup>4</sup> Not available.

<sup>5</sup> Estimate.

<sup>6</sup> U.S. imports.

Florida sands being dredged contain about 4 percent heavy minerals, composed of about 40 percent ilmenite, 4 percent leucoxene, 7 percent rutile, 11 percent zircon, 0.5 percent monazite, and the remainder kyanite and other silicates. Efficient dredging methods and rapid concentration with spiral and pinched-sluice separators have made it profitable to exploit these low-grade, heavy-mineral sands.

Current producers are E.I. duPont de Nemours & Co., Inc., near Starke; Titanium Alloy Manufacturing Division of National Lead Co., South Jacksonville; and the Florida Mineral Co., Vero Beach.

#### Metallurgical

The primary producers of reactor-grade zirconium sponge are U.S. Industrial Chemical Co., Division of National Distillers & Chemical Corp., Ashtabula, Ohio; The Carborundum Metals Co. Division, The Carborundum Co., Parkersburg, W. Va.; Columbia-National Division, Pittsburgh Plate Glass Co., Pace, Fla.; and Wah Chang Corp. Albany, Oreg. Carborundum, Wah Chang, and U.S. Industrial Chemicals Co. produce the hafnium sponge that is converted to crystal bar by Foote Mineral Co., Exton, Pa., and Nuclear Materials & Equipment Corp., Apollo, Pa.

Leading producers of zirconium ingot are The Carborundum Metals Co.; Oregon Metallurgical Corp., Albany, Oreg.; Bridgeport Brass Co., Niles, Ohio; Wah Chang Corp., U.S. Industrial Chemicals Co., and Harvey Aluminum, Inc., Torrance, Calif. Bridgeport Brass, Westinghouse, Wah Chang Corp., and Jessop Steel Co., Washington, Pa., are the major fabricators of zirconium ingot.

Zirconium powder is made principally by Foote Mineral Co., The Carborundum Metals Co., Nuclear Materials & Equipment Corp., and Wah Chang Corp. Union Carbide Corp., Metals Division, Alloy, W. Va. and Ashtabula, Ohio; Vanadium Corporation of America, Cambridge, Ohio; and Titanium Alloy Manufacturing Division of National Lead Co. make most of the zirconium ferroalloys.

#### Refractory and Chemical

Companies processing zircon to refractories and to zirconia and zirconium chemicals are principally in the East and Midwest.

Three companies--The Norton Co., Huntsville, Ala., Titanium Alloy Manufacturing Division National Lead Co., and Harbison-Carborundum Corp., Falconer, N.Y.,--produce most of the zirconium oxide used for nonmetal applications.

Zircon and zirconia refractories are made principally by Corhart Refractories Co., plants at Louisville, Ky., Buckhannon, W. Va., and Corning, N.Y.; Harbison-Carborundum Corp.; the Chas. Taylor Sons Co., Cincinnati, Ohio, and South Shore, Ky.; and Walsh Refractories Corp., St. Louis, Mo.

Most of the zirconium chemicals are produced by Titanium Alloy Manufacturing Division National Lead Co.; Stauffer Chemical Co., Niagara Falls, N.Y.; Kawecki Chemical Co., Boyertown, Pa.; and Titanium, Zirconium Co., Flemington, N.J.

## DOMESTIC ZIRCON PRODUCTION

Recovery of heavy minerals from domestic alluvial deposits is confined, at present, to operations in Florida, where zircon is a coproduct with ilmenite, rutile, leucoxene, and monazite. However, zircon has been produced in Oregon, Idaho, and California as a constituent of heavy sands from stream and beach placer deposits worked primarily for some other mineral.

During the early part of World War II, the urgent need for chromium attracted attention to the black-sand occurrences on the ancient marine terraces along the southwest coast of Oregon. Deposits near Coquille, Coos County, were exploited and, during the short life of the operation, chromite, zircon, and garnet fractions were produced. Later some of this zircon was used by the Bureau to develop the magnesium-reduction (Kroll) process for making ductile zirconium metal.

Prior to 1910, monazite (with associated zircon) was recovered from a placer operation in the Boise Basin, Idaho. In the early 1940's, some zircon was obtained as a byproduct of a dragline operation for gold near Lincoln, Placer County, Calif. No other production of zircon, at least in terms of significant tonnage, has been reported from California. Later, monazite, a rare-earth phosphate mineral containing thorium, was urgently sought for national defense as it was in short supply in this country because of restricted imports from India in 1946 and Brazil in 1955. India was our main source before 1946. An extensive field-exploration program by the Bureau of Mines, sponsored by the Atomic Energy Commission (AEC) from 1948 to 1955, indicated tonnages of monazite that could be made available for industrial and stockpiling purposes, provided the financial incentive was great enough. The first sustained placer dredging in the Pacific Northwest, for other than precious metals, began in January 1951 and continued until about the middle of 1955 on Big Creek near Cascade, Valley County, Idaho. Electrically-operated, converted bucketline gold dredges were used to produce black-sand concentrates containing monazite, ilmenite, zircon, and garnet. A substantial quantity of monazite was produced at the beneficiation plant at Boise and shipped; very little, if any, zircon, found a market. The operation ceased because of a weakened domestic market resulting from large imports of monazite from South Africa.

In the Bear Valley area (Valley County) of the upper reaches of the Middle Fork of the Salmon River, occur relatively large quantities of euxenite (a columbium-tantalum mineral containing titanium, yttrium, certain heavy rare-earth elements, uranium, and thorium) and columbite. The monazite is not as abundant as in the Big Creek area. Exploitation by dredging began late in 1955. Full-scale operation, employing two dredges, was underway early in the following year, and a beneficiation plant was built at Lowman. A Government contract for purchase of more than a million pounds of combined columbium-tantalum oxides provided the incentive. Certain heavy rare earths, uranium, and thorium also were recovered as part of the agreement. Some monazite was marketed. Operations continued until late summer 1959 when the contract terminated. Sizeable tonnages of byproduct zircon, ilmenite, magnetite, and garnet remained at the mill and also at the warehouse in Boise. No zircon was marketed.

Table 2 shows domestic production of zircon and certain metallic and nonmetallic derivatives.

TABLE 2. - Domestic production of zircon and its metallic and nonmetallic derivatives,  
1952-63  
(Tons)

Year	Zircon	Zirconium sponge	Zirconium ingot	Zirconium oxide	Zircon and zirconium refractories	Hafnium oxide	Hafnium sponge
1952	( <sup>1</sup> )	100	( <sup>2</sup> )	( <sup>2</sup> )	( <sup>2</sup> )	( <sup>2</sup> )	( <sup>2</sup> )
1953	23,900	140	( <sup>2</sup> )	121	( <sup>2</sup> )	( <sup>2</sup> )	3.5
1954	16,300	245	( <sup>1</sup> )	676	( <sup>2</sup> )	( <sup>2</sup> )	3.5
1955	28,110	{ 163 reactor grade 25 commercial grade }	( <sup>2</sup> )	( <sup>1</sup> )	( <sup>2</sup> )	( <sup>2</sup> )	3.5
1956	43,980	238	( <sup>2</sup> )	( <sup>2</sup> )	( <sup>2</sup> )	( <sup>2</sup> )	3.5
1957	<sup>3</sup> 56,802	( <sup>1</sup> )	( <sup>2</sup> )	( <sup>1</sup> )	( <sup>2</sup> )	( <sup>2</sup> )	( <sup>2</sup> )
1958	30,443	1,265	( <sup>2</sup> )	( <sup>1</sup> )	( <sup>1</sup> )	( <sup>2</sup> )	<sup>4</sup> 31
1959	( <sup>1</sup> )	1,405	830	( <sup>1</sup> )	16,500	45	17.5
1960	( <sup>1</sup> )	1,423	1,345	6,906	24,862	63	35
1961	( <sup>1</sup> )	1,697	1,405	5,731	20,737	56	( <sup>1</sup> )
1962	( <sup>1</sup> )	1,272	1,282	4,495	37,100	29	( <sup>1</sup> )
1963	( <sup>1</sup> )	1,022	928	5,283	21,000	65	( <sup>1</sup> )

<sup>1</sup> Figure withheld to avoid disclosing individual company confidential data.

<sup>2</sup> Not available.

<sup>3</sup> Florida only.

<sup>4</sup> Includes Hf content of HfO<sub>2</sub>.

#### DOMESTIC ZIRCON RESOURCES

Occurrences of zircon and other heavy minerals are widespread in the Northwest States and in California and Alaska. Many alluvial deposits contain limited quantities of zircon which could be recovered as a byproduct or coproduct with other valuable minerals such as euxenite, monazite, columbite, ilmenite, magnetite, and garnet.

The following economic appraisal of the zircon resources of Idaho, Montana, Oregon, Washington, California, and Alaska was made from information gathered during investigations by the Bureau of Mines. Much of the current information was obtained from unpublished data gathered by one of the authors. Reconnaissance data tables have been published for Montana and Idaho as part of a series of titanium minerals study. (22, 48.)

#### Idaho

Exploration and reconnaissance samples taken by the Bureau indicate that recoverable quantities of zircon occur in certain Idaho placer deposits.

Much of the following information concerned with the zircon resources of Idaho has been compiled from Bureau sample data accumulated during previous studies made of these deposits (14, 48).

In Idaho the known potential zircon resources are located in seven stream drainages (table 3)(fig. 1). The deposits with the highest potential are within the Payette, Boise, and Upper Salmon River drainages.

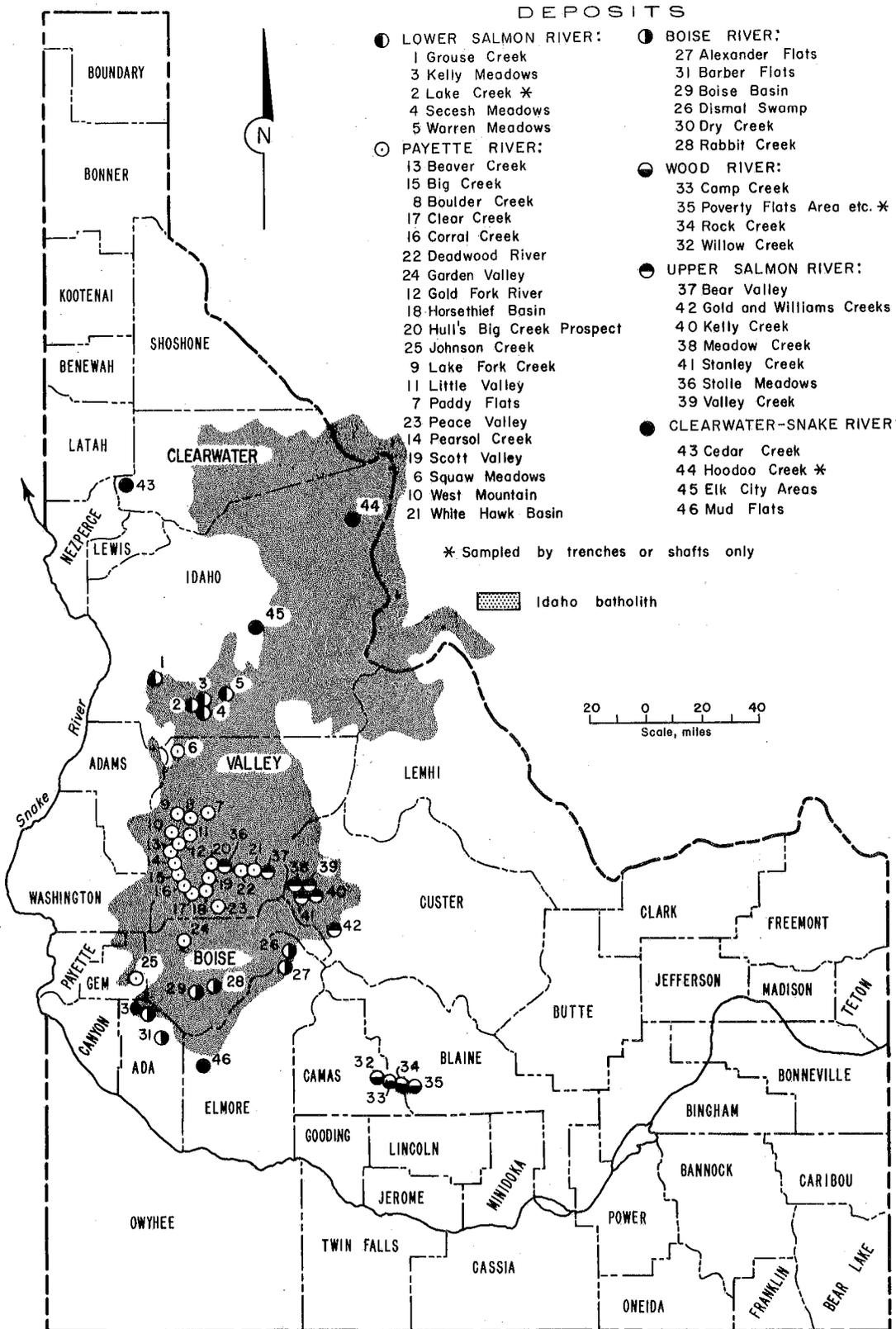


FIGURE 1. - Deposits Sampled by Drill Holes, Trenches, or Shafts.

TABLE 3. - Zircon resources of Idaho<sup>1</sup>

River drainage	Number of deposits <sup>2</sup>	Zircon, thousand short tons	Estimated volume, million cubic yards
Payette River.....	16	147.6	1,015
Boise River.....	7	35.9	129
Wood River.....	2	4.6	26
Upper Salmon River.....	5	46.2	441
Lower Salmon River.....	4	15.0	100
Clearwater-Snake River.....	5	30.3	145
Total.....	39	279.6	1,856

<sup>1</sup> Indicated and inferred resources estimated from Bureau of Mines exploration sample data.

<sup>2</sup> Deposits with more than 1,000 tons.

The deposits with more than 1,000 tons of potential zircon content are listed in table 4. Placer areas examined by reconnaissance methods are shown on figure 2.

Zircon has been reported as abundant in the black-sand concentrates from many placers in the State. Such information can be misleading, unless it is realized that in most cases the black-sand content of the deposit is quite low. This is especially true in the Warren and Florence areas of Idaho County where the heavy mineral concentrates often contain more than 10 percent zircon. Dwight Schmidt, in his study of Valley County (44), states "Zircon is considered abundant when it exceeds 0.01 percent of the rock." Schmidt also reported that "Zircon occurs in all the rock types. It is most abundant in the McCall migmatite and least abundant in the Warm Lake quartz monzonite." Thus, there is good reason for the higher concentration of zircon in the area south of McCall in Long Valley.

#### Payette River Drainage

The Payette River and its tributaries drain the southwestern part of the Idaho batholith. Included in the drainage area are 15 deposits in Valley County and the Garden Valley deposit in Boise County (see table 4 and figure 1). Most of the deposits are in the Long Valley district, and from early 1951 until mid-1955, the first large-scale dredging operations for black sands in Idaho were undertaken in this district. Principal activity was centered at Big Creek 3 miles south of Cascade.

Four of the deposits--Big Creek (T 13 N, R 4 E), Gold Fork River (Tps 15 and 16 N, Rs 3 and 4 E), Little Valley (T 16 N, R 4 E), and Scott Valley (T 14 N, R 4 E)--contain 90,000 tons of the potential zircon resources. The other deposits include: Beaver Creek (T 14 N R 4 E), Boulder Creek (T 17 N, R 4 E), Clear Creek (Tps 12 and 13 N., Rs 4 and 5 E.), Corral Creek (T 13 N, R 4 E), Garden Valley (Tps 8 and 9 N), Rs 4 and 5 E), Horsethief Basin (T 14 N, R 4 E), Lake Fork Creek (Tps 17 and 18 N, R. 3 E), Peace Valley (T 12 N, R 6 E), Pearsol Creek (Tps 13 and 14 N, R 4 E), Squaw Meadows (Tps 14 and 15 N, R 6 E), West Mountain (Tps 15 and 16 N, R 3 E).

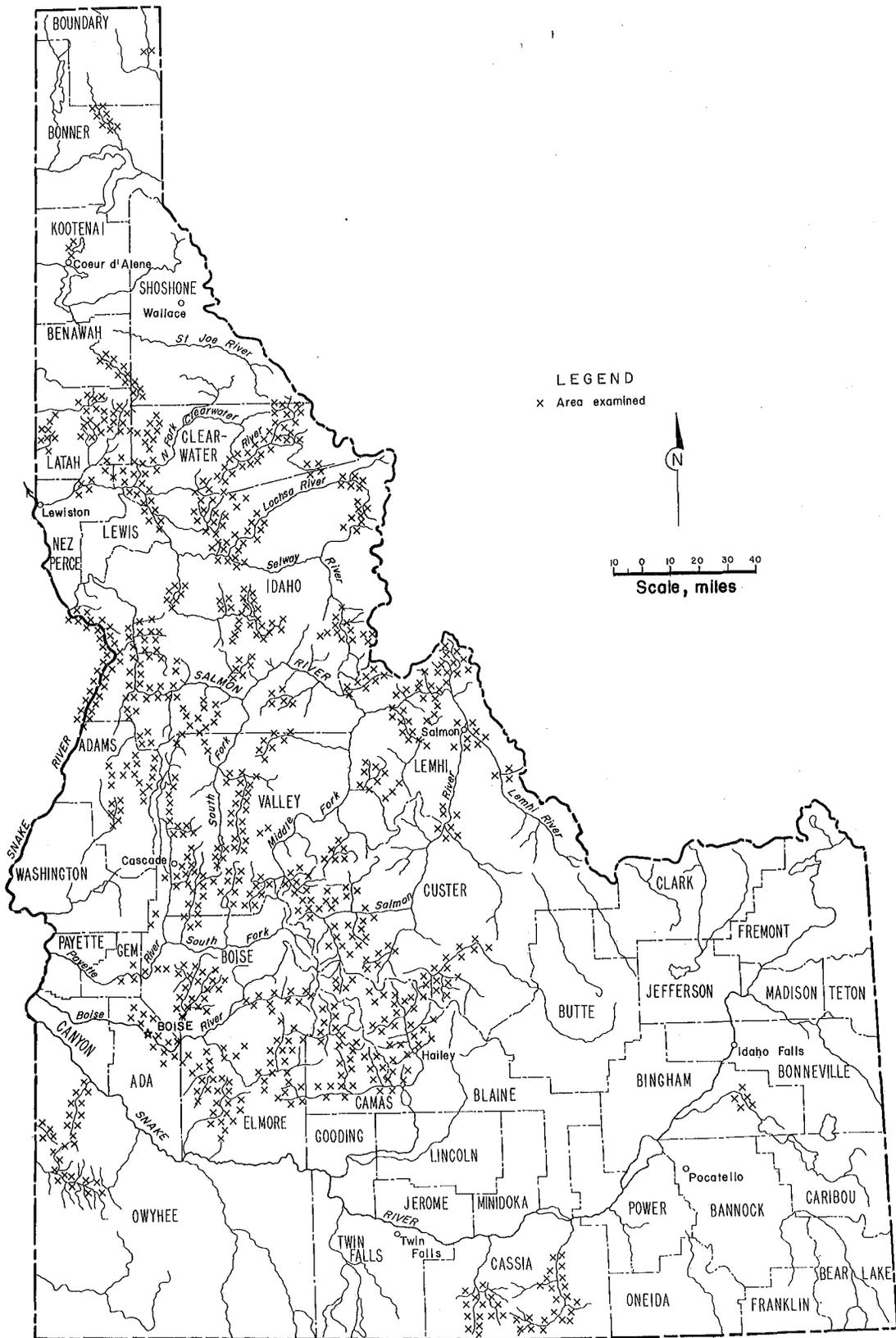


FIGURE 2. - Placer Areas Examined by Reconnaissance Methods.

TABLE 4. - Exploration data for accessory black-sand minerals  
in Idaho placer deposits

Deposits	County	Black sand lb/cu yd	Mineral content lb/cu yd				
			Zircon	Monazite	Ilmenite	Magnetite	Garnet
Payette River drainage							
Beaver Creek.....	Valley	15.64	0.10	0.51	10.60	0.50	0.10
Big Creek.....	..do..	19.96	.62	1.50	13.40	.20	1.50
Boulder Creek.....	..do..	42.25	3.59	Trace	19.20	2.77	3.52
Clear Creek.....	..do..	11.42	.30	.71	4.60	.30	5.00
Corral Creek.....	..do..	8.13	.10	1.80	3.90	.20	.10
Deadwood River.....	..do..	9.92	.09	.08	3.28	4.57	.45
Garden Valley.....	Boise.	6.51	.10	.18	1.65	.30	2.90
Gold Fork River.....	Valley	19.64	.33	.38	10.30	4.00	2.90
Horsethief Basin.....	..do..	8.22	.40	1.57	3.10	.30	.30
Lake Fork Creek.....	..do..	11.3	.30	Trace	2.10	2.42	3.32
Little Valley.....	..do..	22.65	.45	.45	6.80	6.90	5.60
Peace Valley.....	..do..	7.49	.28	.29	1.63	2.92	2.20
Pearsol Creek.....	..do..	14.7	.19	.84	9.93	.50	0.58
Scott Valley.....	..do..	15.21	.70	.57	9.10	.60	1.90
Squaw Meadows.....	..do..	4.65	.36	.16	2.04	1.22	.41
West Mountain.....	..do..	4.58	.09	.06	2.56	.36	.17
Boise River drainage							
Boise Basin:							
Fall Creek.....	Boise.	8.84	0.72	0.63	2.42	4.73	0.34
Granite Creek.....	..do..	8.13	1.25	.96	2.97	2.21	.74
Grassy Flats.....	..do..	4.32	.43	.34	1.75	1.67	.15
Grimes Creek.....	..do..	4.78	.61	.61	1.82	1.25	.49
Moores and Elk Creeks.	..do..	2.71	.52	.19	0.45	.08	1.47
Wolf Creek.....	..do..	7.45	1.69	.83	3.15	1.18	.60
Dry Creek.....	Ada...	4.05	.28	.08	2.00	.30	.10
Wood River drainage							
Camp Creek.....	Blaine and Camas	21.47	0.31	Trace	4.13	9.40	Trace.
Rock Creek, Area 1.....	Blaine	20.91	.45	Trace	3.34	7.37	Trace.
Upper Salmon River drainage							
Bear Valley:							
Upper.....	Valley	29.26	0.07	0.83	13.80	3.70	7.90
Central.....	..do..	13.65	.04	.60	6.90	3.20	1.10
Lower.....	..do..	9.53	.23	.10	3.70	2.10	.70
Gold and Williams Creeks	Custer	33.34	.20	.89	3.51	25.26	Trace.
Stolle Meadows.....	Valley	10.82	.77	.15	2.12	5.30	1.50
Lower Salmon River drainage							
Lake Creek.....	Idaho.	8.8	0.40	-	-	-	-
Secesh Meadows.....	..do..	5.75	.54	0.30	1.61	0.8	1.49
Warren Meadows:							
Bench Ground.....	..do..	1.89	.08	.31	0.19	.27	.57
Valley Ground.....	..do..	2.60	.13	.34	.18	.21	.81
Clearwater River drainage							
Elk City Areas:							
Big Elk Creek.....	Idaho.	11.83	0.37	0.32	7.03	0.51	0.28
Central Red River.....	..do..	16.81	.69	.41	5.13	5.24	.37
Upper Red River.....	..do..	14.87	.56	.35	4.27	3.93	.30
Hoodoo Creek.....	..do..	63.37	1.00	Trace	52.16	2.30	.70
Snake River drainage							
Mud Flat.....	Elmore	8.98	.14	0.24	0.83	1.48	4.40

Sufficient water for dredging is available in the immediate vicinity of all the deposits except the Corral Creek deposit where the nearest adequate supply is about 2 miles away.

Power transmission lines are on or near all of the deposits with exception of the deposits at Squaw Meadows, Peace Valley, and the Deadwood River. All but these three deposits are also within 10 miles of a branch line of the Union Pacific Railroad between Emmett and McCall. Access to the deposits is by way of well-maintained, hard-surfaced or improved roads.

The Boulder Creek deposit, 2.5 miles east and 1 mile north of Lake Fork, has the highest average zircon content of any placer tested in Idaho. The deposit is thin and covers about 160 acres in a shallow depression near the eastern edge of Long Valley. Exploration consisted of two 15-foot churn-drill holes.

#### Boise River Drainage

There are two placer areas in the Boise River drainage that can be considered sources of zircon. Black sand from the Boise Basin area of Boise County contained the highest percentage of zircon of any concentrate tested by the Bureau in Idaho, or in any of the other Northwest States. Concentrates from the Dry Creek placer deposit in Ada County contained an abundance of zircon. The Alexander Flats and Dismal Swamp placers in Elmore County and the Barber Flats area in Ada County had trace amounts of zircon. The Rabbit Creek placer in Boise County contains appreciable gold but has a low zircon potential.

Boise Basin includes six placer deposits (Grassy Flats, Wolf Creek, Fall Creek, Granite Creek, Grimes Creek, and Moores Creek-Elk Creek). These deposits are north and west of Idaho City on streams tributary to the Boise River, in Tps 6, 7, and 8 N, Rs 4, 5, and 6 E, of the Boise Meridian.

There is over 28,000 tons of potential zircon in the Boise Basin area. Boise Basin has been the scene of both large- and small-scale placer operations for many years. Intermittent placer-mining operations still exist in the area.

Zircon content of the black sands ranges from 8 to 23 percent in 4.3 to 8.8 pounds of recoverable black sand per cubic yard as indicated by Bureau sampling in 1949. (See footnote 6). Monazite content of the gravel ranges from 0.19 to 0.96 pound per cubic yard. Approximately 90 percent of the minable gravel in Boise Basin has been dredged, hydraulicked, or placered by some other method for gold. Most of the black sand values remain to be exploited when the need arises.

The Dry Creek placer deposit is in T 6 N, Rs 1 and 2 E, Boise Meridian. State Highway 15 crosses the deposit 7 miles north of Boise. Grab samples (surface concentration in creeks) contain from 25.4 to 53.6 pounds of black sand per cubic yard. Zircon content ranged from 1.4 to 2.5 pounds per cubic yard. One 50-foot churn-drill hole averaged 4.05 pounds of black sand per cubic yard or 0.29 pound of zircon per cubic yard.

### Wood River Drainage

Five placer areas were examined in the Wood River drainage. They include four placers in Blaine County: Dead Sheep Creek (T 1 S, R 18 E), Poverty Flats (T 1 N, R 18 E), Reed Creek (T 1 N, R 18 E), and Rock Creek (T 1 N, R 16 E, and T 1 S, R 17 E). The Dead Sheep Creek, Poverty Flats, and Reed Creek deposits are estimated to have a combined zircon resource potential of 1,950 tons. These deposits, in addition to Area 2 and Area 3 of the Rock Creek deposit (43), are not shown in table 4 because potential zircon resources in their respective areas are less than 1,000 tons. The Camp Creek placer area (T 1 N, R 16 E, and T 1 S, R 16 E) is on the boundary between Blaine and Camas Counties. The placers are noncontiguous, and there is not sufficient water in their respective areas to operate conventional dredging equipment with the exception of Rock Creek, where sufficient water is available during the spring and early summer months. Water would have to be obtained from reservoirs during the dry summer months. The abundance of clay in the placer material will make recovery of the black-sand minerals difficult by conventional dredging methods.

Screen analyses on composite samples of black-sand concentrates from Camp Creek indicate that 56 percent of the zircon is minus 200-mesh, which would make recovery quite difficult under other than laboratory conditions.

The deposits in the Wood River drainage contain appreciable amounts of uranothorite (48) in addition to the accessory minerals shown in table 4.

The deposits can be reached by a combination of paved, graveled, and dirt roads from Bellevue, the site of the nearest rail connection to the East (Union Pacific). High-voltage powerlines cross or are within a reasonable distance of all the deposits.

### Upper Salmon River Drainage

There are three placer areas in the Upper Salmon River drainage with potential zircon resources of more than 1,000 tons each. They include the Bear Valley placers (Tps 11, 12, and 13 N, Rs 8, 9, and 10 E) which consist of three contiguous deposits and the Stolle Meadows (T 15 N, R 6 E) in Valley County, and Gold and Williams Creek (T 9 N, R 14 E) in Custer County. The Kelly Creek, Meadow Creek, Stanley Creek, and Valley Creek deposits (48) in Custer County have a low zircon potential.

The Stolle Meadows deposit is included in the Upper Salmon drainage; however, it is in the upper valley of the South Fork of the Salmon River. Access is by Forest Service road, and there is sufficient water but no nearby power or rail transportation.

The Bear Valley placers--Upper Bear Valley (Big Meadows), Central Bear Valley, and Lower Bear Valley--are in the Boise National Forest. Bear Valley is an upland valley trending north-south and circuted by Bear Valley Creek which flows northward approximately 6.5 miles through the upper and central portions of the valley before trending northeastward and passing through Lower Bear Valley before joining the headwaters of the Middle Fork of the Snake River.

Porter Brothers Corp. dredged in the area from late 1955 to November 1959 and produced a black-sand concentrate containing euxenite as the major constituent.

The Gold and Williams Creek placer is 9.5 miles south of Stanley. U.S. Highway 93 crosses the western edge of the placer. Ketchum, 70 miles farther south, is on a branch line of the Union Pacific Railroad. There is abundant water, and the character of the gravel makes it suitable for dredging. Power is available at the deposit.

#### Lower Salmon River Drainage

Five placer areas, all in the Lower Salmon River drainage of Idaho County, were explored by churn drilling, shafting, or trenching. Included are Lake Creek (T 22 N, R 4 E), Grouse Creek (T 25 N, R 4 E), Kelly Meadows (T 23 N, R 5 E), Secesh Meadows (T 22 N, R 5 E), and Warren Meadows (Tps 22 and 23 N, R 6 E). Water is abundant in all the areas.

The Secesh Meadows on the Secesh River is potentially a good zircon source. The gold and monazite values are relatively high and would have a good resource value, if the need ever arises.

Warren Meadows and Lake Creek have a fair resource potential for zircon.

Grouse Creek and Kelly Meadows do not contain sufficient heavy minerals to be considered for dredging. It is interesting to note that Grouse Creek concentrates contain an average of 15 percent zircon, but the concentrates average only 1.2 pounds per cubic yard.

#### Clearwater River Drainage

The Elk City areas (Tps 27 and 28 N, R 9 E, and T 29 N, R 8 E) and the Hoodoo Creek placer (Tps 34 and 35 N, Rs 14 and 15 E), both in Idaho County, were evaluated in the Clearwater River drainage. Both placers have a good resource potential.

The Elk City placer is comprised of three separate deposits--Big Elk Creek, Central Red River, and Upper Red River--north and east of Elk City, Idaho, a town with some considerable fame as a gold mining center. There is abundant water, and the area is served by well-maintained roads. Power has recently been brought to the area.

The Hoodoo Creek placer (48), on the headwaters of the Locksa River, a tributary of the Middle Fork of the Clearwater River, is important as a source of zircon and ilmenite. Remoteness is a major drawback to production of black-sand minerals from this area at the present time.

#### Snake River Drainage

Many placers were sampled by reconnaissance methods in the Snake River drainage; however, only one was drilled to determine its black-sand content.



FIGURE 3. - Placers Examined in Montana.

The Mud Flats deposit (T 1 S, R 6 E) in Elmore County has limited potential as a source of zircon.

Montana

Placer deposits examined in Beaverhead, Granite, Ravalli, and Silver Bow Counties, contain an estimated 44,000 tons of zircon in 344 million cubic yards of placer material. Titaniferous sandstone in Glacier, Pondera, and Teton Counties contain an average of 5 pounds of zircon per ton and represent

another 50,000 tons of the mineral. All of these figures are estimates; therefore, further drilling may prove or disprove them.

Reconnaissance sampling data from more than 225 stream areas throughout western Montana, including exploration data on 8 placer deposits that were explored in some detail, were used in compiling the potential zircon resources of the State (22).

Zircon occurrences are widespread in Montana placer deposits; however, as in other areas, the mineral can only be considered as a potential byproduct of other black-sand production. Concentrations of zircon average less than 1 pound per cubic yard in all of the placer deposits examined (fig. 3).

Exploration work, done by the Bureau on eight deposits, comprised churn drilling, trenching, and test pitting. In all, 83 holes were churn-drilled, totaling 3,201 linear feet; 28 trenches were excavated, totaling 305 feet in depth; and 24 test pits were dug, totaling 115 feet in depth.

#### Bitterroot River Drainage

The Bitterroot River and its tributaries drain all of Ravalli County and the southwest part of Missoula County. The area is served by a branch line of the Northern Pacific Railway and by U.S. Highway 93.

The results of reconnaissance sampling in the Bitterroot River drainage area indicated trace amounts to less than 0.5 pound of zircon per cubic yard of placer material in those areas where estimates were made for zircon content.

The Victor deposit, 35 miles south of Missoula by U.S. Highway 93 and  $\frac{1}{2}$  mile west of Victor, is accessible throughout the year by improved county roads.

Exploration work consisted of 45 churn-drill holes ranging in depth from 10 to 100 feet and totaling 2,186 feet.

An average of three screen analyses of concentrates from composited drill-hole samples indicated that more than 40 percent of the material was minus 100-mesh, and that this fraction contained 62 percent of the monazite values, and about 80 percent of the zircon.

Black-sand values are unevenly distributed and may occur as residual concentrations in alluvium or in gravel interbedded with lenses of clay.

Average content of the black sand was 9.6 pounds per cubic yard, including 0.31 pounds of zircon, 2.3 pounds of ilmenite, and 0.65 pounds of monazite. Table 5 presents exploration data. Three selected areas, representing about 14 percent of the total deposit, averaged 0.37 pounds of zircon, 4.6 pounds of ilmenite, and 1.13 pounds of monazite per cubic yard. Table 6 shows a petrographic analysis of a sample of composited concentrates.

TABLE 5. - Exploration data for some accessory black-sand minerals in Montana placer deposits

Deposits	County	Black sand lb/cu yd	Mineral content, lb/cu yd				
			Zircon	Monazite	Ilmenite	Magnetite	Garnet
Bitterroot River drainage							
Cameron Creek	Ravalli...	18.8	0.26	0.49	11.0	2.5	0.28
McCalla Creek	...do.....	20.72	0.37	1.37	4.64	8.96	1.70
Rye Creek....	...do.....	20.0	0.19	<sup>1</sup> 0.12	3.6	11.93	0.15
Victor.....	...do.....	9.6	0.31	0.65	2.3	2.9	.39
Upper Clark Fork River drainage							
Powder Gulch.	Silver Bow	44.45	0.57	<sup>2</sup> Trace	6.48	25.29	Trace
Price Gulch..	...do.....	36.00	0.70	<sup>2</sup> Trace	8.20	19.39	Trace
Sand Basin...	Granite...	59.03	0.25	( <sup>3</sup> )	6.02	35.42	2.36
Jefferson River drainage							
Trail Creek..	Beaverhead	11.27	0.05	0.22	5.03	4.03	0.17

<sup>1</sup> This figure does not include other radioactive minerals.

<sup>2</sup> The chief radioactive mineral was tentatively identified as thorite.

<sup>3</sup> Values were expressed in monazite equivalent.

Source: Holt, Dean C. Titanium Placer Resources in Western Montana. BuMines Rept. of Inv. 6365, 1964, 39 pp.

TABLE 6. - Petrographic analysis of composited concentrates from drill hole 13, Victor

Mineral	Percent	Mineral	Percent
Ilmenite.....	15	Xenotime.....	0.5
Monazite.....	12	Rutile.....	Trace
Magnetite.....	24	Sphene.....	4
Epidote and other ferromagnesian minerals....	17	Zircon.....	2
Quartz.....	19	Unidentified opaques.....	1
Garnet.....	5	Radioactive opaques.....	Trace
		Pyrite.....	Trace

The McCalla Creek deposit is 4 miles north of Victor and west of U.S. Highway 93. Preliminary sampling of surface gravels indicated a high monazite content. Three widely spaced holes from 30 to 45 feet in depth were drilled.

Black-sand content, averaging 21 pounds per cubic yard, included 0.37 pounds of zircon, 4.6 pounds of ilmenite, and 1.37 pounds of monazite per cubic yard.

This amount of drilling was insufficient to warrant conclusions as to the size and grade of the deposit.

The Rye Creek deposit, 4½ miles south of Darby on U.S. Highway 93, is served by an improved gravel road.

Exploration work consisted of 10 churn-drill holes with an aggregate depth of 510 feet. Holes ranged from 23 to 88 feet in depth; eight reached bedrock.

The deposit encompasses the lower 5½ miles of Rye Creek Valley, about 200 acres in area.

Black-sand concentrates ranged from 2 to 65 pounds per cubic yard in the 5-foot drill samples. Zones containing the highest concentrations of heavy sands ranged from 5 to 35 feet in thickness. The highest concentrations of black sand were found below depths of 20 to 45 feet in the five downstream holes and 5 to 10 feet in the upstream holes. Average content of the black sands was 20 pounds a cubic yard, and zircon averaged 0.2 pounds. Mineralogical analyses of two preliminary samples showed an average of 1.5 percent zircon and 1 percent rutile in the concentrates.

The Cameron Creek deposit is accessible by 2 miles of graveled road northeast of Sula on U.S. Highway 93. The placer, about 5 miles long and averaging 300 feet in width, extends along the valleys of Cameron Creek and its tributaries, Hart Creek and Doran Creek.

Exploration consisted of grab samples from six test pits 2 to 4 feet in depth and two channel samples from drainage ditches 7 to 10 feet in depth. Bedrock was not reached.

Black-sand concentrates consist principally of ilmenite and smaller amounts of garnet, zircon, magnetite, and monazite. The samples contained an average of 11.0 pounds of ilmenite, 0.5 pounds of monazite, and 0.27 pounds of zircon per cubic yard.

#### Upper Clark Fork River Drainage Area

The Upper Clark Fork River drainage area includes deposits within the Clark Fork River Basin from Missoula upstream to the headwaters of Silver Bow Creek southeast of Butte. Among the major tributary streams in the basin are the Blackfoot River, Rock Creek, Flint Creek, Little Blackfoot River, and Silver Box Creek. The area includes all of Granite County and parts of Deer Lodge, Missoula, Lewis and Clark, Powell, and Silver Bow Counties. Reconnaissance data showed a trace to less than 0.5 pounds of zircon per cubic yard in those areas tested for the mineral. Three deposits were explored in some detail, and a summary of the sample results is shown in table 5.

Price Gulch is in the Siberia or German Gulch mining district in Silver Bow County. The area may be reached from Butte by traveling 6½ miles west on U.S. Highway 10S to Silver Bow, then 2 miles southwest on a county road to its junction with a farm road which leads to the deposit.

Exploration consisted of 16 trenches ranging from 3 to 19 feet deep; all but two reached bedrock. About 84 acres of creek, bench, and residual placers were explored.

The Powder Gulch deposit is  $1\frac{1}{2}$  miles southeast of Price Gulch, and is accessible throughout the year.

Exploration consisted of 12 trenches ranging from 7 to 20 feet in depth. All the trenches bottomed in hardpan.

The Sand Basin deposits are in Granite County on the West Fork of Rock Creek near the crest of the Sapphire Mountains. A mine road extends to the property from State Highway 38 at a point 27 miles southwest of Philipsburg, or 38 miles east of Hamilton. The area is normally inaccessible in winter and early spring because of heavy snowfall.

In 1954, the Bureau of Mines cut 19 samples from 18 prospect pits or shallow test holes. The depth of the deposits was not determined.

Presence of many large granite boulders probably will prevent mining in the narrow valleys between the deposits by conventional dredging methods.

#### Jefferson, Madison, and Gallatin River Drainages

The Jefferson, Madison, and Gallatin Rivers join below the town of Three Forks to form the Missouri River.

Essentially all of the favorable creek bed and bench placer areas of tributary streams were tested for black-sand deposits. Several of the areas contain large amounts of black sand, but no economic concentrations of zircon were found (table 5).

Reconnaissance sampling in the Jefferson River drainage indicated the absence of potentially valuable zircon deposits; however, the Trail Creek placer deposit in the Big Hole Basin, which was sampled for monazite by churn drilling, had some zircon in the black-sand concentrates.

Less than 0.1 pound of zircon per cubic yard was indicated by reconnaissance sampling in the Madison River drainage.

In 23 samples taken in the Gallatin River drainage, the heavy mineral content ranged from 2 to 8 pounds per cubic yard with trace amounts of zircon reported (22).

Baddeleyite and zircon have been identified as accessory minerals in the Bozeman corundum deposits near Bozeman, Mont. (20). The baddeleyite occurs as grains in and along the crystals of corundum. The grains of baddeleyite resemble rutile in form.

The most significant deposit in this region is on Trail Creek, a major tributary of the North Fork of the Big Hole River. The deposit covers an area more than 14 miles long and 50 to 700 yards wide. It can be reached by State Highway 43 from Wisdom, Mont., which is 11 miles from the lower end of the deposit. The deposit is essentially a gold placer.

Exploration work by the Bureau consisted of 25 churn-drill holes ranging from 9 to 33 feet deep and totaling 400 feet. A summary of the exploration data is given in table 5. There is ample water for dredging.

The black-sand minerals in the coarse gravels above bedrock clay are about twice as abundant as in the overlying alluvium. Table 7 shows a petrographic analysis of a sample of composited concentrates.

TABLE 7. - Petrographic analysis of composited concentrates, Trail Creek

Mineral	Percent	Mineral	Percent
Ilmenite.....	44.6	Pyrite.....	0.8
Magnetite.....	35.8	Sphene.....	.4
Monazite.....	2.0	Zircon.....	.2
Garnet.....	1.5	Allanite.....	.2
Epidote.....	1.2	Quartz-feldspar.....	11.3
Other ferromagnesian minerals	1.0		

#### Yellowstone River Drainage

A small amount of reconnaissance sampling was done on the Yellowstone River and its major tributary streams in Park and Sweetgrass Counties directly north of Yellowstone National Park. The estimated black-sand content of the placer material ranged from a trace to 15 pounds per cubic yard. Magnetite was the major heavy mineral constituent in all of the concentrates; only trace amounts of zircon were recovered.

#### Missouri River Drainage

The Missouri River and its tributaries drain all of Montana east of the Continental Divide except the northeastern corner of Glacier National Park.

None of the placer deposits examined can be considered a potential source of zircon. The best concentration of black-sand minerals was found on the Prickly Pear Creek drainage in Jefferson County south of Helena. Alluvial sands there contained from 2 to 20 pounds of black sand per cubic yard; ilmenite ranged from 3 to 10 percent, magnetite from 60 to 90 percent, and only trace amounts of zircon.

In Glacier, Pondera, and Teton Counties, titaniferous magnetite deposits of sedimentary origin occur as irregularly distributed lenses in sandstone beds of late Cretaceous age (62). Stream beds in and around many of these deposits were sampled quite thoroughly. The deposition of black-sand minerals in recent stream gravels derived partially from indurated sandstone was found to be minor as compared to the black-sand content of the sandstone itself. The fineness of the titaniferous materials and the immaturity of the stream drainages have precluded the formation of new black-sand placer deposits in the area.

Stebinger (46) reported that the titanium oxide present in sandstone samples ranged from 6.8 to 12.8 percent. Samples taken during a Bureau study

being made on the iron resources of the Northwest showed similar results. Many of the individual deposits are found along many ocean beaches in Oregon and Washington. Beneficiation tests on samples taken from deposits in Glacier and Teton Counties showed an average of 0.25 percent recoverable zircon.

#### Lower Clark Fork River Drainage

The lower Clark Fork drainage area includes deposits within the Clark Fork River Basin downstream from Missoula to the Idaho State line. The basin includes all of Flathead, Sanders, Mineral, and Lake Counties and parts of Missoula and Powell Counties. Flathead River, the major tributary stream, drains most of the area.

Reconnaissance sampling data indicate the absence of any significant zircon or titanium minerals in the placer deposits.

#### Kootenai River Drainage

The Kootenai River drainage comprises all of Lincoln County in northwestern Montana. Main access to the area is provided by U.S. Highway 2 and the Great Northern Railroad. Most of the stream areas are accessible by State, county, and Forest Service roads; unimproved dirt roads reach some of the more remote properties.

Reconnaissance sampling of alluvium from several of the larger tributary streams showed a very low black-sand content and only trace amounts of zircon.

#### Oregon

Black-sand deposits along the Oregon coast have a fair zircon potential providing that coproduct chromite can be upgraded into a salable product. Reconnaissance sampling by the Bureau indicated a low potential for zircon in Oregon stream placer deposits; zircon content ranged from trace amounts to 0.7 pound per cubic yard of gravel.

#### Black Sand Beach and Terrace Deposits

The better deposits are in Coos County (fig. 4). Deposits with the highest potential for zircon are listed in table 8, and the deposits of limited size are listed in table 9. Their locations are shown on figure 5. The total potential resource is estimated to exceed 90,000 short tons of zircon.

TABLE 8. - Analysis of some black-sand deposits of southwestern Oregon, Coos County

Name	Mineral content, percent		
	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>5</sub>	ZrO <sub>2</sub> <sup>1</sup>
Shepard mine.....	3.1	20.8	1.9
Section 33 deposit.....	0.8	26.3	0.9
Butler mine.....	2.7	23.8	0.9
Eagle mine.....	6.5	43.1	3.0
Pioneer mine.....	3.1	48.8	2.5
Seven Devils mine <sup>2</sup> .....	4.8	24.1	1.7
South Slough Region.....	6.3	8.3	1.4

<sup>1</sup> Approximate amount of zircon in the area is 67,000 tons.

<sup>2</sup> Composite of four samples from mine.

Source: U.S. Geol. Survey Bull. 945E, 1945, 37 pp.

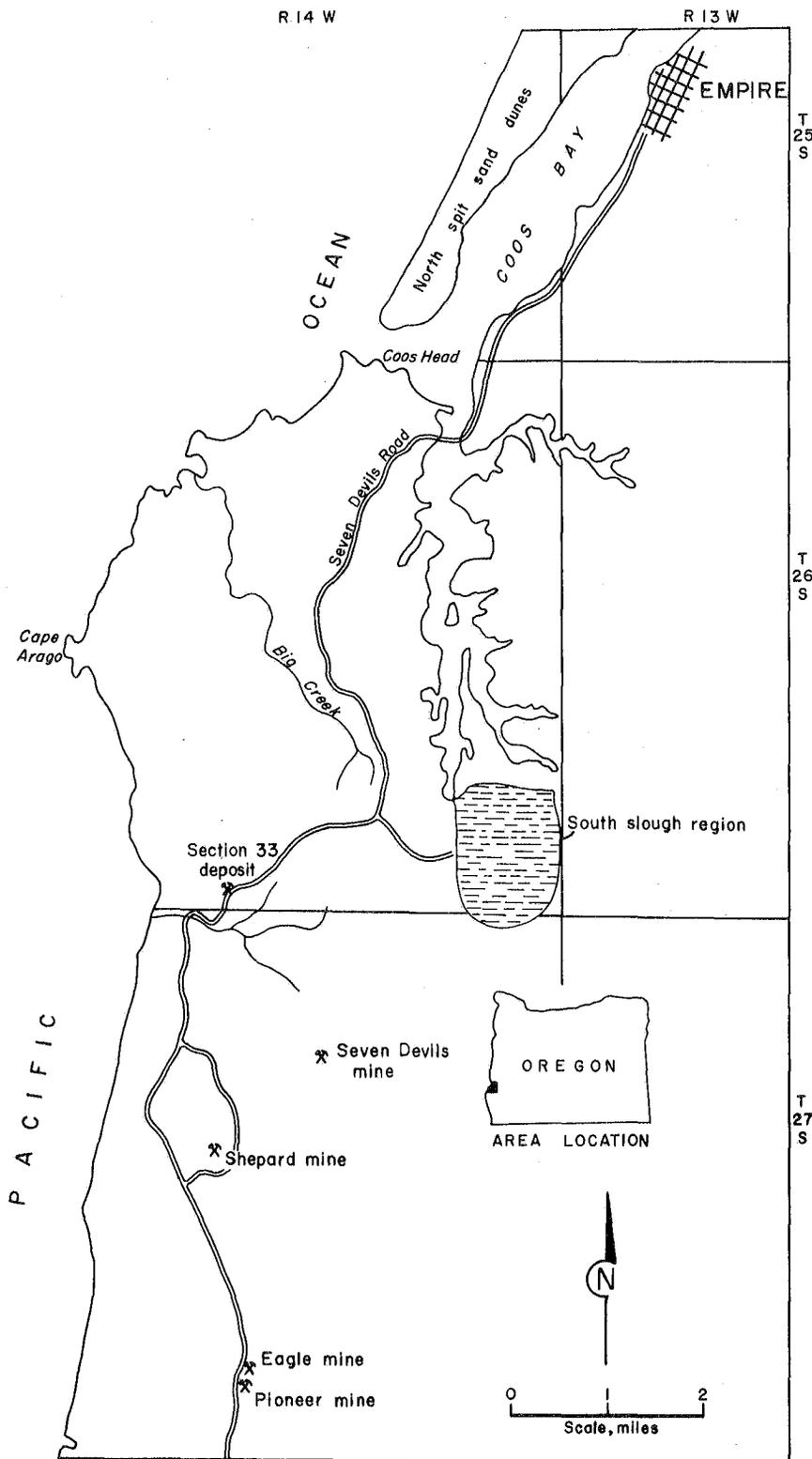


FIGURE 4. - Selected Beach Sand Deposits in Coos County, Oreg.

Much data have been published concerning the extent and origin of Oregon black-sand deposits.

Most geologists concede that the black sands have been derived from the disintegration of basic igneous rocks. According to Diller, these rocks underlie wide areas in southern Oregon and northern California (13).

The original deposits of black sands range from 0.25 percent up to, but seldom exceeding, 2 percent and are distributed throughout the mass of the deep gravel beds (28).

Due to the action of the wind and tides, the concentration of the black sands on the present ocean beaches is erratic and constantly changing. The deposits are lenticular in shape and are made up of interstratified layers of black sand and lighter materials.

Ancient beach deposits are represented by terrace deposits. The largest deposits of black sand are in the three lower terraces, all of which are less than 350 feet above sea level (27). These occurrences are designated by Griggs (18)

as the Seven Devils Terrace, Pioneer Terrace, and the Whiskey Run Terrace. Other terraces are only erosional remnants and are not known to contain important deposits of black-sand minerals.

TABLE 9. - Selected beach-sand deposits along the Oregon coast, Coos Bay to the mouth of the Columbia River (high tide level)<sup>1</sup>

Location	County	Ilmenite plus chromite, pct	Zircon, pct	Magnetite, pct	Remarks
T 22 S, R 12 W	Lane.....	14.60	0.55	8.55	
T 18 S, R 11 W	..do.....	14.35	2.65	4.25	Lean black sand.
T 17 S, R 12 W	..do.....	6.80	0.73	1.80	Do.
T 18 S, R 12 W	..do.....	5.60	0.37	0.50	Do.
T 16 S, R 12 W	..do.....	37.24	3.72	14.48	Small deposit.
T 16 S, R 12 W	..do.....	37.65	3.50	6.85	Estimated 400 cu yds present.
T 15 S, R 12 W	..do.....	42.80	2.15	6.80	Small deposit.
T 13 S, R 12 W	Lincoln..	54.93	4.47	4.90	Do.
T 12 S, R 11 W	..do.....	11.50	0.35	1.00	Estimated 1,000 cu yds present.
T 11 S, R 11 W	..do.....	55.00	3.20	14.74	Estimated 2,000 cu yds of black sand present.
T 10 S, R 11 W	..do.....	39.15	3.70	10.20	Rich black sand; estimated 1,000 tons zircon.
T 11 S, R 11 W	..do.....	31.50	1.50	2.53	Estimated 12,500 cu yds present.
T 3 S, R 10 W	Tillamook	52.04	1.84	3.12	Small deposit.
T 2 S, R 10 W	..do.....	43.95	2.10	8.40	Do.

<sup>1</sup>Total estimated tonnage from these deposits is between 15,000 and 20,000 tons of zircon.

Source: Reference 53.

The Shepard and Section 33 terrace deposits were operated during World War II to produce chromite. Some 2,100 long tons of a rough zircon concentrate was produced as a byproduct from chromite operations. Subsequently this material was upgraded.

Day and Richards (11) collected and analyzed more than 200 samples from Oregon stream and beach placer deposits during their investigation in 1905. Many of these samples indicated the presence of zircon in substantial amounts. It must be remembered that the samples were taken chiefly for the purpose of locating platinum deposits and that many of the samples represent sluice-box concentrates or surface concentrations of beach sands. A thorough study of their results substantiated work done by the Bureau which indicated a low overall zircon content in stream placer deposits. Their study also indicated the highest zircon content in beach sands was found to exist in the Bandon-Coos Bay area.

In 1943, Twenhofel made an investigation of the black-sand deposits along the Oregon coast from Coos Bay to the mouth of the Columbia River (53). During this

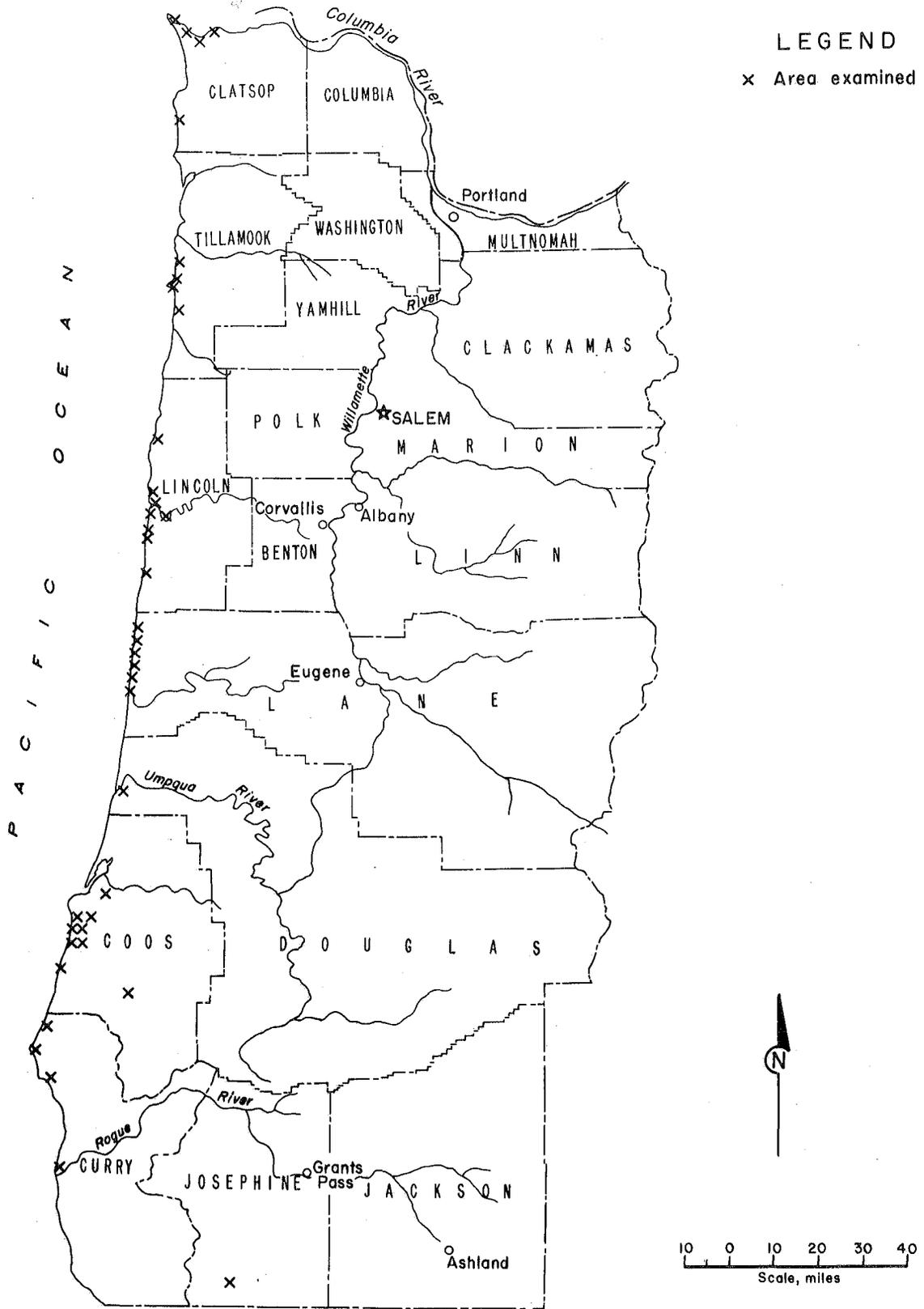


FIGURE 5. - Selected Beach Sand Deposits on the Oregon Coast.

investigation, numerous samples were taken for laboratory testing and analysis. This study showed that black-sand deposits north of Coos Bay are small and quite superficial.

The zircon content of black-sand deposits in the mouth of the Columbia River averages less than 0.3 percent in black-sand concentrates (11). Dredge samples taken by the Bureau in 1950 showed that run-of-the-river sands contained less than 0.03 percent zircon.

The Bureau investigated black-sand deposits near Hammond, Clatsop County, in the estuary of the Columbia River (29).

Large deposits of black sand are known to exist near Fort Stevens, on Clatsop Spit, Clatsop County. These deposits are being considered presently for their potential value as a source of low-cost magnetite (iron ore) for domestic and foreign consumption. Zircon content of the sands in this area averages less than 0.5 pound per cubic yard.

#### Washington

Extensive reconnaissance sampling of most beach and stream placer deposits and limited exploration of two beach deposits indicate a small zircon potential for Washington (fig. 6). Surface concentrations of zircon are on most Washington beaches. The relative amount of zircon in concentrates increases progressively from a trace to 0.3 percent in black sands at the mouth of the Columbia River; northward, along the beach, the content increases to 46 percent in superficial surface concentrations at Ruby Beach in Olympic National Park (16). A black-sand lens in a spit in Grays Harbor, Grays Harbor County, averaged 3 percent zircon. Recoverable reserves of zircon in Washington beach deposits are estimated to be more than 6,000 tons.

#### Grays Harbor Beach Sand Deposit

The deposit is in the North Bay area of Grays Harbor, Grays Harbor County. Exploration samples were taken by means of jet drilling to depths ranging from 7.5 to 44 feet. Drilling was stopped because of lack of values and inability to penetrate barren lenses because of gravel beds.

A sandspit in Armstrong Bay was the only area found to contain important concentrations of heavy minerals. This sandspit at the time of the sampling program, averaged 5,000 feet long and 500 feet wide. Having been formed by action of the wind, tide, and waves, the sandspit is continually shifting its location in the harbor.

The heavy minerals occur in surface lenses in the beach sands. The lenses are crossbedded, and their thickness ranges from 5 to 10 feet with an overall average of 6 feet. The black-sand content of the samples from these lenses ranged from 76 to 870 pounds per cubic yard with an average of 272 pounds per cubic yard. Petrographic studies showed an average of 3 percent zircon in the concentrates.

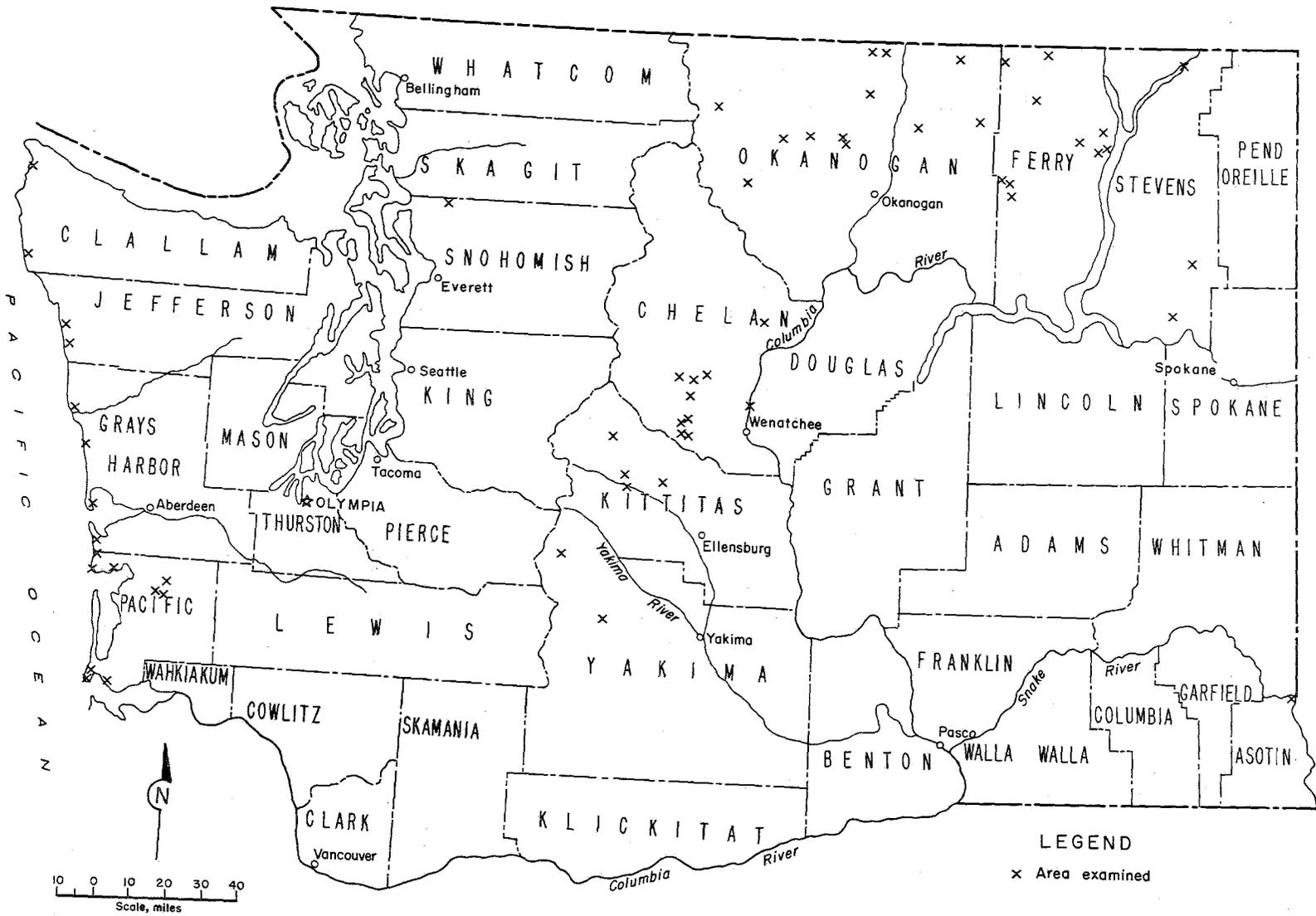


FIGURE 6. - Location of Beach and Stream Placers in Washington.

### McGowan (29)

The McGowan deposit is on the north bank of the Columbia River about 10 miles southeast of Ilwaco. Exploration in 1944 consisted of 49 hand-auger holes with a combined length of 390 feet. This work showed a black-sand lens 2,400 feet long and 400 feet wide with an average thickness of 4.5 feet. Petrographic examination of a black-sand concentrate sample showed a zircon content of 0.3 percent.

### Fort Canby--Beard's Hollow

Recent work indicates reserves of more than 500,000 tons of black sand containing 0.3 percent zircon exist in the Fort Canby--Beard's Hollow Area several miles north of the mouth of the Columbia River.

The reader is invited to review the following literature (3, 7, 11, 30, 40, 61) for more detailed information on Washington zircon resources.

### California

Churn drilling and other placer exploration techniques used by the Bureau in testing eight placer areas in California during 1949 and 1950 indicated a low zircon potential. Total recoverable zircon reserves were estimated at 59,000 tons. Average zircon content of the material tested ranged from a trace to 0.17 pound per cubic yard. Seven of the placers had been or were being mined for gold.

### Hammonton Placer Area

The Hammonton placer along the Yuba River in Tps 15 and 16 N, Rs 4 and 5 E, Mt. Diablo Meridian, Yuba County, contained trace amounts of zircon.

### Waterford Placer Area

The Waterford Placer in Tps 3 and 4 S, Rs 11, 12, and 13 E, on the Tuolumne River, Stanislaus County, contained about 0.15 pound or zircon per cubic yard. The zircon represented an average of 2.5 percent of the black sands.

### Beach Sands

Beach sands were tested in the vicinity of the Monterey Peninsula, Monterey County, and only small amounts of zircon were reported in the concentrates.

### Folsom Field

The Folsom field includes the area above and below the town of Folsom on the American River in Sacramento County. The gravels contained less than 0.05 pound of zircon per cubic yard.

### Merced River

Placers in Tps 4 and 5 S, Rs 13, 14, and 15 E, on the Merced River in Merced County, contained about 0.05 pound of zircon per cubic yard.

### Stanislaus River

Placers on the Stanislaus River immediately downstream from Knight's Ferry in Stanislaus County, contained about 1 percent zircon in 17.1 pounds of black sand per cubic yard. This indicated 0.17 pound of zircon per cubic yard.

### Calaveras River

A placer on the Calaveras River, in Calaveras and Stanislaus Counties, contained a trace of zircon in the black-sand concentrates, which were also low.

### Mokelumne River

The Mokelumne River placers were sampled near where the river crosses the boundaries of Amador, Calaveras, and San Joaquin Counties. The average zircon content of these placers was 0.13 pound per cubic yard.

The black-sand content of all eight of these placers ranged from 3 to 17 pounds per cubic yard; the zircon represented a trace to 2.5 percent.

The only reported production of zircon in California came from a dragline dredging operation near Lincoln, Placer County, in 1937 and 1941. Small quantities were shipped for experimental purposes in both years.

Comments on the zircon content of California placer and beach sand deposits by Day and Richards (1906) (11, pp. 1177-1258), Allen (1929) (1), and in various California Department of Natural Resource Publications (45, 46, 63) are in general agreement--the concentration is too low to permit commercial recovery at prices that have prevailed.

Table 10 shows an incomplete summary of the results of work done by Day and Richards (11).

For example, under Yuba County the results are shown for only one sample. This sample, taken at Camptonville on the Yuba River, contains 40 pounds of zircon per ton of black sand. The source gravels contained only 1 pound of black sand per cubic yard. Seven other samples cited by Day and Richards (11, pp. 1190-1191), show nil to 4 pounds of zircon per ton of black sand. Evaluation of the reference material indicates the lack of zircon potential in the Yuba drainage. In Nevada County, a sample was taken at Nevada City from an old river channel by Day and Richards. This sample, reported to contain 928 pounds of zircon per ton, was obviously obtained from an enriched black-sand lens. It is reasonable to believe that the Ionian Sea formed black-sand lenses somewhat similar to those on our present day ocean beaches. Allen (1, table 1, p. 375) shows the relative percentage of minerals in the heavy sand taken from the Ione formation. In the samples examined, the percentage of minerals heavier than bromoform specific gravity ranged from 0.1 to 1 percent. Zircon was listed as very common in all 10 samples, and ilmenite was abundant. Zircon was considered abundant by Schmidt (44) when it represented over 0.01 percent of the rock.

TABLE 10. - Concentration of zircon in black-sand samples  
from placer deposits in California

Locality	Zircon (lbs/ton of black sand)	Remarks
Butte County:		
Nimshew.....	1	
Oroville.....	48	
Do.....	4	Black sand from dredge clean-up.
Sterling City.....	22	Concentration not known.
Do.....	52	Black sand from sluice box.
Cherokee.....	20	Old tailing dump (fine sand), panning.
Do.....	372	Pannings from old dump.
Do.....	230	
Little Rock Creek.....	184	Very plentiful; ground sluicing.
Brush Creek.....	20	4 lbs black sand per cu yd of gravel.
Calaveras County:		
Douglas Flat.....	64	Concentrated from 60 tons to 100 lbs.
Wallace.....	128	Concentration not known.
Del Norte County:		
Crescent City.....	44	Natural sand, not concentrated.
Do.....	20	Natural sand, not concentrated.
Gilbert Creek.....	1	Natural sand, not concentrated.
Do.....	19	Heavy tailings from sluice box.
Smith River.....	18	Heavy tailings after gold removed by sluicing.
El Dorado County:		
Brownsville district....	80	1 lb of black sand from 7 cu yds gravel.
Placerville.....	176	
Grizzly Flats.....	16	1 lb of black sand per ton gravel; sluicing.
Humboldt County:		
Gold Bluff.....	17	Selected streak of beach sands.
Do.....	17	Tailings from above.
Do.....	3	Ordinary beach sand.
Do.....	2	Beach sand.
Do.....	6	Beach sand.
Do.....	16	Beach sand.
Do.....	6	Beach sand.
Do.....	10	Beach sand.
Do.....	14	Concentrated by panning beach sand.
Upper Gold Bluff.....	12	Beach sand concentrates.
Orleans.....	4	Heavy sand in sluice boxes.
Trinidad.....	80	Beach sand, 3 feet below surface.
Los Angeles County: Ocean Park.	2	Beach sand.
Mendocino County:		
Fort Bragg.....	34	Not concentrated.
Do.....	5	Do.
Nevada County:		
Rough and Ready.....	14	Concentration not known.
Do.....	50	Heavy sand from hydraulic clean-up.
Nevada City.....	928	Old river channel.

TABLE 10. - Concentration of zircon in black-sand samples  
from placer deposits in California--Continued

Locality	Zircon (lbs/ton of black sand)	Remarks
Placer County:		
North Fork American River	340	50 lbs black sand per ton of gravel.
Gold Run.....	192	0.5 lb black sand per cu yd gravel.
Do.....	202	0.5 lb black sand per cu yd gravel.
Plumas County:		
Spanish Ranch.....	20	9 lbs black sand per ton of gravel.
Rock Island Hill.....	88	Concentration not known.
Riverside County: Holcomb.	40	12 lbs black sand per cu yd gravel.
Sacramento County:	316	Concentration not known.
Michigan Bar.		
San Luis Obispo County:	30	Natural sand.
Beach sand.		
San Francisco County:	2	
Beach sand.		
San Mateo County: Beach	100	Natural sand.
sand.		
Santa Barbara County:		
Point Sal.....	54	Not concentrated.
Do.....	94	Concentrated from sluice box.
Santa Cruz County:		
Aptos.....	26	Natural sand.
Do.....	18	Do.
Do.....	22	Do.
Do.....	24	Do.
Shasta County:		
French Gulch.....	24	Concentration not known.
Redding.....	40	0.5 lb black sand from 5 tons gravel.
Do.....	32	Concentration not known.
Siskiyou County:		
Callahan (Grouse Creek).	50	1 lb black sand from 16 cu yds ground sluicing.
Cecilville.....	6	Concentration not known.
Forks of Salmon.....	140	Waste material from clean-up.
Sawyers Bar.....	60	Pannings from sluice-box tailings.
Scott River.....	50	1 lb black sand from 10 cu yds gravel.
Trinity County:		
Trinity Center.....	100	Concentration not known.
Burnt Ranch.....	350	4.5 lbs black sand per cu yd gravel.
Junction City.....	32	Hydraulic tailings.
Carrville.....	25	40 lbs black sand per ton of gravel.
Yuba County: Camptonville	40	1 lb black sand per 3 cu yd of gravel.

Table 11 from Stinson (47) shows the zircon content of sand from recent streams in the San Joaquin Valley. No data are given on how these results were obtained. If these samples were obtained from surface concentrations of the stream placers, the results could be much too high for the average content of stream gravels in this area (31).

TABLE 11. - Approximate amount of zircon in sand from recent streams in the San Joaquin Valley

Stream	Total heavies in sand, percent	Zircon in heavies, percent	Pounds of zircon per ton of sand
San Joaquin River.....	6.60	0.288	0.38
Kings River.....	14.35	0.812	2.4
Kaweah River.....	11.31	0.574	1.26
Tule River.....	15.41	0.511	1.58
Deer Creek.....	8.35	0.232	.38
Poso Creek.....	6.05	3.24	3.92
Kern River.....	7.19	0.616	.89
Do.....	23.59	1.406	7.2
Salt-Tecuyah Creek.....	2.0	3.136	1.26
Plieto Creek.....	3.94	2.205	1.66
San Emigdio Creek.....	7.96	1.556	2.48
Sandy Creek.....	10.72	4.491	9.62

Source: Reference 39, page 709.

### Alaska

Field investigations of alluvial placers and beach-sand deposits by the Bureau of Mines indicate that known zircon resources in Alaska have a low potential. Examinations to date have been of a reconnaissance nature, and less than 5 percent of the total area has been covered.

#### Hot Springs District, Central Alaska (50)

A spectrographic analysis of concentrates from Deep Creek, Hot Springs district, shows zirconium to be present in amounts ranging from 1 to 5 percent. This reduces to about 0.3 pound per cubic yard of recoverable zircon.

#### Beach Sands, Eastern Gulf of Alaska (51)

Zircon is listed as a trace mineral in beach sands along the eastern Gulf of Alaska. Petrographic studies of the nonmagnetic portion of 68 samples show zircon to be present in 60 of them in amounts ranging from trace to a "small amount."

#### Cape Mountain District (39)

Spectrographic analyses of a churn-drill concentrate from the Cape Creek area showed zirconium to be present in amounts ranging from 0.001 to 0.01 percent.

A petrographic analysis of seven churn-drill concentrates from Boulder Creek showed zircon to be a trace mineral in only two samples. A composite sample from these seven churn-drill holes was given a spectrographic examination which showed zirconium to be present in amounts ranging from 0.01 to 0.1 percent.

#### Beach Sands, Bristol Bay, Alaska (4)

Petrographic analysis of 247 samples from the Bristol Bay area shows zircon to be present in trace amounts in 191 of the samples.

#### SAMPLING BEACH SAND DEPOSITS

The most feasible method for testing beach sand deposits is by water-jet drilling. Costs of \$0.68 per foot (42) are very reasonable compared with standard churn-drill sampling costs which usually average more than \$4.00 a foot.

Samples taken by jet drilling in the Grays Harbor area of Washington were somewhat smaller than normally desired. As a consequence, one of the authors developed a weighted method for making composite drill hole and field samples from black sands that had been concentrated from fractions of unequal size and weight. The fractions also contained varying amounts of concentrates.

It was determined, by numerous volumetric and specific gravity tests of samples from the Grays Harbor beach area, that for every percent of concentrate in the sands the weight of the original material increased by approximately 25 pounds per cubic yard, compared with the weight of a barren sample. For example, sands from the Armstrong Bay area of Grays Harbor, containing a trace of concentrate, weighed about 2,500 pounds per dry cubic yard, and similar material from the same area containing 20 percent concentrate weighed 3,000 pounds per dry cubic yard. Dry black-sand table concentrate weighed 185 pounds per cubic foot (about 5,000 pounds per dry cubic yard).

Example of compositing--From a sample weighing 4.06 pounds, the smallest sample used in the field composite, 0.312 pound, or 7.7 percent, was recovered as a black-sand concentrate. This heavy product was split into fractions weighing 0.162 and 0.150 pounds, respectively. The smallest fraction was used in the composite, and the other was saved for possible future study. To determine the quantity of black-sand concentrate that should be taken from each drill-hole sample to make a representative composite, the weight of concentrate, in pounds, per percentile unit was calculated by dividing the weight of the split, 0.150 pound, by 7.7 percent, the percentage of heavy minerals in the drill hole sample. By multiplying the resulting value, or factor, of 0.0195 pound of concentrate per percentile unit by the percent of concentrate recovered from each drill hole sample, it is possible to determine the quantity of black sand required to make the composite. This method of calculation also simplifies making composite drill-hole samples from equal length drill-hole sections.

## MINING AND MILLING

Commercially, zircon is recovered as a coproduct with other minerals, including ilmenite, rutile, monazite, and gold, from a relatively few stream-placer and beach-sand deposits throughout the world. Minor zircon production has come from consolidated rock deposits--sandstone and pegmatite, Ashland, S.C., and pegmatite, Henderson County, N.C., and central Wisconsin.

In the United States, the earliest production came from the Henderson County deposit. A relatively small tonnage was recovered at intervals from 1896 to 1916. Shortly thereafter, beach sands in the vicinity of Mineral City, near Jacksonville, Fla., were worked for ilmenite. Zircon was an unmarketable product at that time. Subsequently, development of zircon opacifiers provided a market for the zircon output until mining ceased in 1928. In 1943, the Rutile Mining Co. began to recover ilmenite and rutile from the ancient dunes near Jacksonville. The tailings that contained the zircon were stockpiled for possible future separation. Eventually these stocks were processed, and the new interest in zircon has resulted in a steady increase in domestic production since 1945.

Most heavy sand mining is done with electrically-operated bucketline or suction dredges. The bucketline dredge is essentially a floating washing plant equipped with a digging ladder, upon which moves an endless chain of buckets. The length of the digging ladder determines the depth to which the dredge can dig, and size of the buckets determines its capacity. A hydraulic or suction dredge recovers the alluvial material through a pipe lowered on a ladder to the area to be mined. A centrifugal pump is used to create a strong flow of water which causes the sand particles to be sucked off the bottom and to be carried to the surface. A strong jet of water or a power-driven rotary cutter affixed to the end of the ladder breaks up loosely consolidated sediments.

When using a bucketline dredge, the initial concentration usually takes place on the decks of the boat. The dredge concentrates then are pumped ashore, either to a separation plant or for transportation to such a plant. Material recovered with a suction dredge, in most cases, is pumped through a pipe to either a floating or fixed separation plant.

The high specific gravity of the commercial minerals contained in the sands permits separation by gravity-concentration methods. Hydraulic classifiers, shaking tables, and spiral and pinched-slucice concentrators are most suitable for discarding the lighter gangue minerals. Primary gravity separations can be made, using wet feed, with a pinched-slucice concentrator. Using this method, pulp flows into and down a narrowing chute. As the charge courses downward, the pulp segregates, and the heavy minerals settle to the bottom. At the end of the chute, the pulp is split into various fractions.

After drying the bulk concentrates, various fractions are recovered by magnetic and electrostatic methods. Minerals have a wide range of magnetic susceptibility. Thus effective separations can be made by passing mixtures through fields of varying intensity. Electrostatic and high-tension processes

of separation are based upon the electrical properties of minerals. By their nature, minerals are either conductive or nonconductive. Thus by attracting or repelling, separation of the minerals can be accomplished.

Zircon producers in Australia sometimes have difficulty removing fine-grained quartz by wet methods. Recent work (25) has indicated that air tabling may be more effective and more economical. The main difference between an air table and a wet shaking table is that a current of air through openings in the deck is used in place of cascading water to classify the feed.

Froth flotation is used quite widely by Australian producers to recover zircon and other heavy mineral products. Flotation consists of agitating in a small tank or cell, a mixture of ore, sand-size or finer, with water containing one or more reagents until a froth forms. By selectively coating the mineral grains to make them either water avid or water repellent, separations can be effected. The water repellent particles will attach themselves to the bubbles in the froth, rise to the surface, and can be removed by scraping the froth off the top of the cell.

#### Florida (33-34)

Recovery and beneficiation of Florida sands involve suction dredges, pinched-slucice and spiral concentrators, and magnetic and electrostatic separators.

In April 1949, a plant at Trail Ridge started operation. About 1,300 tons of beach sand is mined per hour with a 20-inch suction dredge. Organic debris and hard clay made it necessary to install a revolving cutting head on the end of the suction pipe. The dredge output is pumped to the separation plant about 700 feet away. The entire plant is very portable because virtually all of the processing equipment is mounted on pontoons. A total of 1,100 Humphreys spirals is used in the wet-separation process--704 in the rougher stage and 264 and 132, respectively, in the cleaner and recleaner stages. Feed from the dredge is dewatered by bowl and rake classifiers, to a pulp containing 35 to 40 percent solids before going to the spirals. The spiral concentrates are pumped ashore to a scrubbing plant where they also are dewatered. Then the thickened pulp is scrubbed to remove foreign matter, again dewatered, and sent to the stockpile. From here the concentrates are passed through 2 driers before going to the high-tension separators, which are modifications of electrostatic separators but differ because there is a high current flow (at 40,000 volts) between the electrode and rotor. There are 28 rougher, 12 cleaners, 4 residue-cleaner, and 16 scavenger high-tension rotors. Also used in the circuit are four 10-rotor induced-roll magnetic separators. The high-tension equipment separates the most conductive titanium-group minerals from less conductive zircon, monazite, and quartz. A magnetic separator divides the titanium-mineral fraction into ilmenite and arizonite and nonmagnetic rutile. The tailing product from the high-tension step, which contains zircon and small quantities of ilmenite and other heavy minerals, is pumped to the zircon-recovery plant. Here the product is respiraled, dewatered, calcined, and passed over the high-voltage separators. Four 4-rotor high-tension separators and two 10-rotor induced-roll magnetic separators are used in this plant. The zircon product is sacked and shipped to market.

### Idaho (2)

Electrically operated, converted bucketline gold dredges on Big Creek in Cascade Valley, Valley County, produced black-sand concentrates containing monazite, ilmenite, zircon, and garnet. Only monazite was marketed; the other minerals were accumulated as concentration rejects.

Baumhoff-Marshall, Inc., in September 1950 started operating a 6-foot dredge in the area. It had an 80-foot digging ladder and eighty 6-cubic-foot buckets and could reach 35 feet below the water level. Average capacity per 24-hour period was 5,000 cubic yards. Late in the summer of 1951, Idaho-Canadian Corp. put into operation a dredge of the same size and capacity, but the digging ladder was 13 feet longer, there were four more buckets, and it could reach a depth of 45 feet. About the same time, the Warren Dredging Corp. started operating a 4-cubic-foot dredge in the same area.

The separation procedure was similar on the 6-foot dredges. The buckets emptied into a 6- by 48-foot trommel screen having plates drilled with 3/16- and 1/4-inch round holes. Undersize flowed to double jigs arranged on each side of and at right angles to the trommel. With this arrangement, recovery was increased because all sand flowed across two cells. The resulting rougher concentrates were dewatered, then cleaned by two jigs of the same type. A 400-cubic-foot storage tank amidships held the finished product until it was pumped ashore.

Treatment of the concentrates before trucking to Cascade differed. The product from the Baumhoff-Marshall dredge was pumped directly to a 10-ton dump truck on the bank. Idaho-Canadian pumped from the dredge to a V-screen with 24-mesh screen cloth. Oversize (nearly all ilmenite) was discarded, and undersize went to a 3-foot dewatering cone. The thickened pulp was pumped to a 25-ton steel loading bin. Concentrates from both operations were trucked to Cascade and stored separately while awaiting shipment by rail to Boise.

At the concentration plant in Boise, the sand was dried in a rotary kiln and passed over high-intensity and magnetic separators. The monazite was bagged and shipped to processors. An ilmenite-magnetite-garnet fraction and a zircon-quartz fraction were stored awaiting possible retreatment into usable products if a market were provided. (See flow sheet, fig. 7.)

The Warren Dredging Corp. operated its dredge until May 1953, when an accident caused it to capsize.

Porter Bros. Corp. operated two connected bucketline dredges (6-cubic-foot and 4½-cubic-foot capacity) in the Bear Valley area, Valley County, from 1955 through August 1959.

The dredges produced black-sand concentrates containing euxenite, columbite, monazite, garnet, ilmenite, magnetite, and zircon (38).

The concentrates were shipped to Lowman, Idaho, by truck where high-grade euxenite, columbite, and monazite concentrates were produced by magnetic and electrostatic beneficiation methods. The remaining black-sand minerals were stockpiled for later sale when markets developed (12).

### Oregon (24, 28)

The urgent need for chromium during the early part of World War II drew attention to the black-sand occurrences on the ancient marine terraces along the southwest coast of Oregon. After extensive exploration, the Krome Corp. was organized to exploit the deposits in the Seven Devils district about 17 miles south of Marshfield. Mention of the operation is intended to illustrate another method for mining and

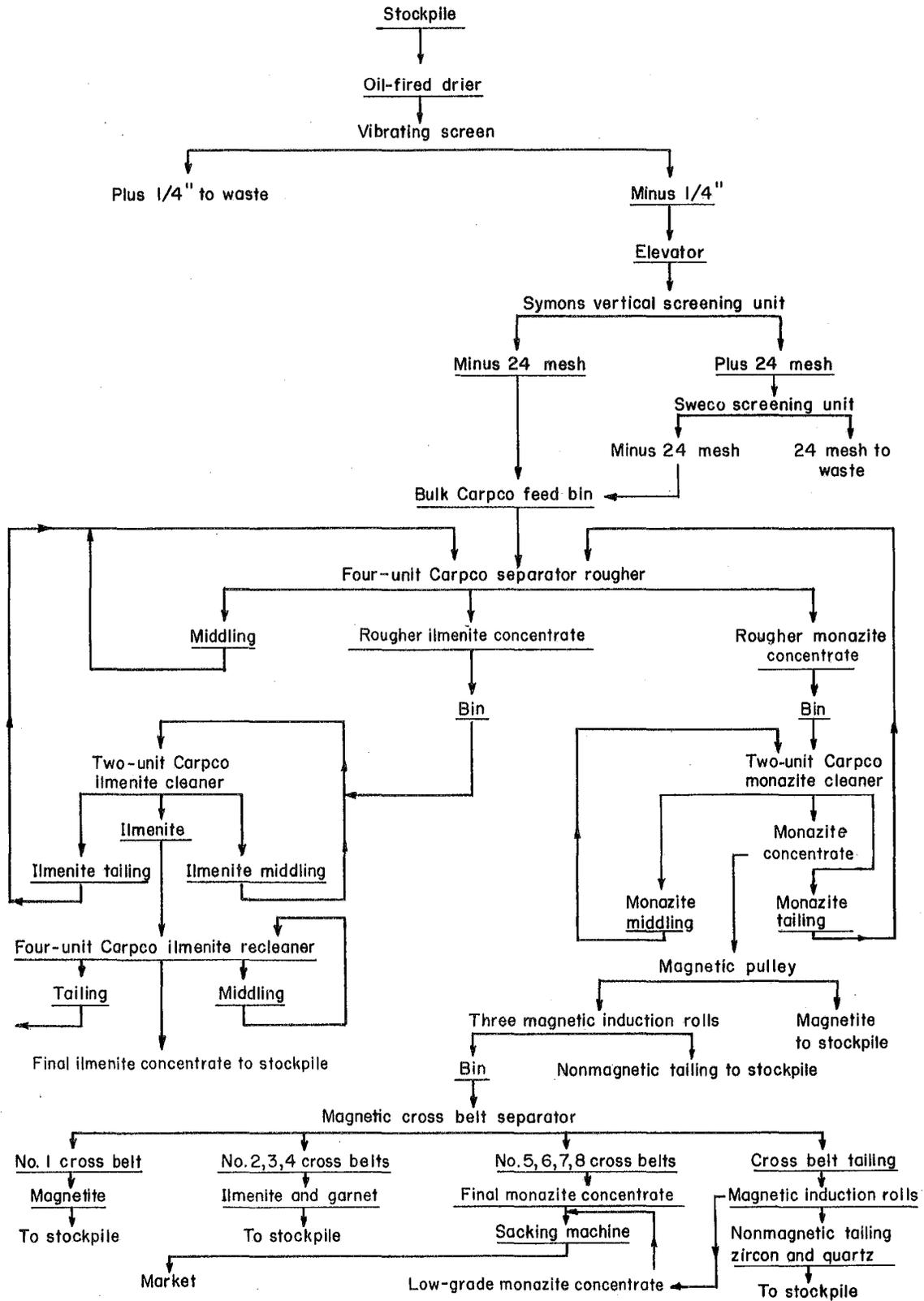


FIGURE 7. - Baumhoff-Marshall, Inc., Black Sand Separation Plant Flowsheet.

milling beach and terrace sands. Although chromite was the primary product, substantial quantities of zircon were recovered and stockpiled.

It was planned originally by the Krome Corp. to install a wet gravity concentrator near the mine, which would produce a low-grade bulk concentrate. This product was to be processed at a magnetic-separation plant near the railroad at Beaver Hill. Carryalls and scrapers were to be used for removing the overburden, and mining was to be done with power shovels. The ore proved to be quite soft, and carryalls were used almost exclusively for the entire operation. A slackline with a 6-cubic-foot scraper was tried on several occasions.

The ore was treated by wet-separation methods. Wet screens, rolls, and rod mills were used to disintegrate and scrub the material before desliming in a hydroseparator. About 6 tons of Unclassified feed per hour was put over large deck tables; the middlings were sized and retabled. The bulk concentrate from the tables was collected in a sump and pumped to a cone ahead of a four-cell flotation unit, which functioned as a scrubber to remove the last traces of adhering slime. In the final step, the cleaned bulk product (containing about 35 percent  $\text{Cr}_2\text{O}_3$  and a substantial quantity of zircon) was dewatered and belt-conveyed to a concrete storage platform to await trucking to the magnetic plant.

The Southwestern Engineering Co. built and operated the magnetic concentrator at Beaver Hill for the Defense Plant Corporation. Here the dried bulk concentrate was separated into various fractions by progressive stages of magnetic intensity. After passing through an indirect oil-fired chemical drier, the concentrate was put over a vibrating screen to remove any tramp material present and was carried by a screw conveyor to 100-ton storage bins which fed five induced-roll-type magnetic separators. A highly magnetic fraction containing magnetite, ilmenite, and high-iron garnet was removed by the first pass over the rolls. The tailing from this pass was distributed to three high-intensity separators to yield four chrome products and two offgrade products. Rejects from this operation were put over a special magnetic separator to produce another chrome product and a tailing composed chiefly of zircon with smaller quantities of minerals of low magnetic susceptibility. This product was treated on a crossbelt separator, resulting in two chrome products and zircon-rich tailing. All chrome fractions were combined and transported to a surge bin ahead of the flotation department. After conditioning, the garnet was removed in a six-cell flotation unit. The chrome product (tailing) was dewatered, dried, and stockpiled. The zircon-bearing fractions were put over tables to produce a high-grade product by removing silica. A small quantity of rutile remained. The zircon product was dewatered, dried, and sent to storage.

#### Australia (10, 35, 41)

Suction dredging is the universal method of mining alluvial sands in Australia. The quantity of sand mined and the nature of the deposits have not justified the high capital cost of bucket dredges.

In most of the Australian operations, dredge concentrates are pumped through rubber hoses to fixed beneficiation units. The others have the dredge

pumps mounted on the same barge as the concentrating units. At one operation on the east coast of North Stradbroke Island, dredge concentrates are conveyed 7 miles by aerial tramway to a separation plant on the other side of the island.

Dredge concentrates usually are reworked at a "wet plant" before going to the separation plant. Shaking tables, which were used quite widely before 1953, have been replaced by methods capable of handling large tonnages more effectively. Tables now are used to make selective separations at some intermediate point in the finishing plant. Standard cast-iron Humphreys spirals are still used by some operators. Variations of the original spirals made of concrete, plastic, and fiberglass also are in use.

Froth flotation has been used since 1934. One company uses flotation to separate zircon from wet-plant concentrates. After drying, the zircon fraction is subjected to high-tension separation, screening, and air-tabling to make a premium-grade product.

#### MINING AND MILLING COSTS

Dredge mining costs may vary somewhat because of the remoteness of the deposit and size of the dredge, also because of local requirements such as the need for land restoration and prevention of stream contamination. Costs of operating bucketline dredges used in mining Idaho black-sand concentrates during the 1950's averaged about \$0.25 per cubic yard. These costs are based on the use of 4½- and 6-cubic-foot bucketline dredges. Milling costs averaged about \$5.00 per ton of black sand beneficiated and separated by magnetic and electrostatic (high-tension) methods.

Total costs of using similar dredges for gold mining would range from \$0.08 to \$0.25 per cubic yard under normal conditions. Dredges of the sizes mentioned cost between \$1.0 and \$1.5 million erected.

An article (15) gives the operating costs of cutter-head hydraulic dredges.

Pumping costs are an important consideration in transporting dredge concentrates. These costs range from \$0.06 per cubic yard through a 10-inch pipeline to \$0.035 through a 30-inch pipeline. An article on pumping phosphate rock through a pipeline a distance of 2 miles lists the cost at \$0.069 (14-inch line) (26). Problems encountered in pumping this material would be quite similar to those encountered in pumping black-sand concentrates.

Treatment plant charges ordinarily would average about \$5.00 per ton of primary black-sand concentrates. Therefore, the foregoing information should give the reader some idea of costs to be encountered in producing black-sand minerals for market.

An alternate mining method which would be applicable to Oregon beach-sand deposits near Coos Bay would be by slackline or dragline. Costs would range from \$0.06 to \$0.15 per cubic yard. The costs of mining the individual black-sand lenses would necessarily be raised after consideration of the charges for removing overburden before mining material considered ore grade.

## HISTORY OF DUCTILE ZIRCONIUM METAL PRODUCTION

The element zirconium was discovered in 1789 by the German chemist Martin Klaproth, now famous for being the first to recognize uranium, titanium, and cerium. In 1824, Jöns Jakob Berzelius (5), a Swedish chemist, made impure zirconium powder from potassium-zirconium fluoride by reducing it with sodium. L. Troost (1865)(52) was the first to reduce zirconium tetrachloride with magnesium. The first malleable zirconium was made by D. Lely and L. Hamburger (32) in 1914. They interacted resublimed zirconium tetrachloride and sodium in a sealed bomb. Other developments followed by Weiss and Neumann (60) and by Marden and Rich (37) until 1925 when A. E. Van Arkel and J. H. DeBoer (55), working at the University of Leyden, introduced the iodide dissociation method. This process, although slow, expensive, and apparently not readily adaptable to large-scale production, was modified for factory operation by Philips Lamp Co., Eindhoven, Netherlands.

The Foote Mineral Co., Philadelphia, Pa., obtained patent rights from DeBoer in 1940 and was the sole producer of ductile zirconium in the United States until Westinghouse Electric Corp. entered the field some years later to help meet the increasing requirements of the Atomic Energy Commission. Westinghouse developed larger furnaces and was able to make crystal bars weighing up to 100 pounds. All of the domestic production of ductile zirconium was made by this process until 1949.

In 1945, as part of its regular program of <sup>延展性</sup> metallurgical research, the Bureau began investigations on ways of making ductile zirconium metal that led to the development of the magnesium-reduction method, which is more economical than the iodide-dissociation process. The Oak Ridge National Laboratory of the AEC requested the Bureau to make a ton of low-hafnium zirconium sheet from Brazilian baddeleyite (low-hafnium content). Research at Oak Ridge indicated that, because of the dissimilar behavior of zirconium and hafnium in the presence of thermal neutrons, low-hafnium zirconium would be required in constructing nuclear reactors (the thermal neutron absorption cross section of hafnium is 600 times that of zirconium). During the time that it took to prepare that much sheet, a need for relatively large quantities of the reactor-grade metal developed, and the AEC and the Department of the Navy, Bureau of Ships, financed expansion of the Bureau of Mines facility through several steps to full-production scale. Concurrently, a method was developed to separate the zirconium and hafnium by solvent extraction.

The Bureau supplied the domestic requirements for ductile zirconium until January 1954 when a commercial plant began producing the metal. Over 1 million pounds of ductile zirconium had been produced at Albany before full responsibility for its production passed from the Bureau to Carborundum Metals Co., Inc., in 1955. Capacity at the Carborundum Co. Akron, N.Y. facility was increased to 325,000 pounds annually early in the following year.

In May 1955, the AEC closed the Bureau plant at Albany after determining that current industrial production plus stocks were sufficient to supply its immediate need for zirconium. The plant, however, was to be put in standby condition to resume operation within 60 days, if required. The atomic-energy

applications of zirconium, heightened by the successful trials of the nuclear-powered submarine, U.S.S. Nautilus, expanded so rapidly that, late in the same year, the Commission took steps to increase the immediate supply of the ductile metal. Industry was invited to bid on operation of the Bureau plant and to build new plants capable of producing 5,500 tons of reactor-grade metal in 5 years. In the interim, negotiations were completed with Japanese interests for 100 tons of zirconium sponge in exchange for surplus agricultural products. Wah Chang Corp. contracted to make 600,000 pounds of reactor-grade sponge over a 2-year period at the Bureau's Albany plant, and three companies concluded 5-year agreements in 1956 to furnish 1,100 tons per year. The following are salient facts:

Company	Location	Plant capacity, tons	Annual quota, tons	Price per lb
U.S. Industrial Chemical Co.	Ashtabula, Ohio...	1,000	500	\$4.53
Columbia-National Corp.....	Pensacola, Fla....	750	350	6.50
Carborundum Metals Co., Inc.	Parkersburg, Va. <sup>1</sup> .	600	250	7.72

<sup>1</sup> New plant; old one at Akron, N.Y., had capacity increased from 200,000 to 325,000 pounds annually.

Ownership of U.S. Industrial Chemical Co., a division of Mallory-Sharon Metals Corp., in 1958 was held equally between National Distillers and Chemical Co., P. B. Mallory Co., Inc., and Sharon Steel Corp., and the name was changed to Mallory-Sharon Metals Corp. In January 1960, Bridgeport Brass Co. assumed management, and in May, National Distillers and Sharon Steel increased their holdings and changed the name to Reactive Metals, Inc. Bridgeport Brass retained management and an option to purchase Reactive Metals shares. The following year, Bridgeport Brass Co. merged with National Distillers and Chemical Co. Currently, as divisions of the distilling company, U. S. Industrial Chemical Co. produces sponge at Ashtabula, Ohio, and Bridgeport Brass Co. makes ingot and fabricates mill products at Niles, Ohio. Reactive Metals Inc. markets the products.

Columbia-National Corp., originally owned by Columbia Southern Chemical Co. and National Research Corp., became a wholly-owned subsidiary of Columbia Southern in 1959.

In 1957, Columbia-National made its first shipments of ductile zirconium, and Wah Chang began operating its own newly completed plant (annual capacity, 1,000,000 pounds) at Albany in addition to the Bureau facility (combined annual production rate of both Albany plants was 900,000 pounds). Shipments by Mallory-Sharon Metals Corp. began in 1958.

Wah Chang Corp. put its plant on stream at Albany in November 1957 and in the first quarter of 1958 completed its contract with the AEC and concluded operation of the Bureau facility. The Commission called for bids to process 65,000 pounds of hafnium oxide to sponge metal over an 18-month period, and Wah Chang Corp. was selected to process the material. Foote Mineral Co. subsequently converted the sponge to crystal bar.

During 1961, the above production facilities yielded output equivalent to 61.5 percent of capacity.

#### HAFNIUM

Hafnium is a ductile, corrosion-resistant metal with a very high neutron-absorption cross section. The element was discovered in 1922 by Coster and Von Hevesy (8) while studying the X-ray spectra of certain zirconium minerals. Urbain (54) claims to have made the same discovery while studying certain rare earths. Von Hevesy showed that hafnium resembles zirconium very closely in chemical properties and that the two elements are associated in nature. They further showed that the two outer electron shells of hafnium should be identical to those of zirconium in the elemental state. Therefore, despite wide differences in atomic weight and density, the chemical behavior should be quite similar. The varying hafnium content of zirconium minerals accounted for the difference in atomic weights assigned to zirconium by early investigators. G. von Hevesy wrote several other informative articles on the new element (56-59).

Hafnium--present in the earth's crust in concentrations about equal to beryllium, uranium, or germanium, and more abundant than tantalum, mercury, columbium, or silver--is isomorphous with uranium and thorium, and as a consequence, a constant ratio is maintained between hafnium and these radioactive elements. The degree of radioactivity of zircon, therefore, is regarded as an index of its hafnium content. Hess (21) showed that the uranium and thorium content varies from 0.38 percent and 1.1 percent, respectively, for unaltered zircon (low hafnium) to 4.3 percent uranium and 8.1 percent thorium for the high-hafnium altered varieties.

Hafnium and zirconium have strongly opposing properties in an environment of thermal neutrons. The neutron capture cross section of hafnium is 105 barns compared with 0.18 barns for zirconium. This tendency to capture slow neutrons is the reason hafnium must be removed from zirconium that is to be used in nuclear reactors, and accounts for the use of hafnium for reactor control rods.

As has been indicated in another section of this report, after the hafnium and zirconium have been separated in the early stages of the metallurgical process, each is reduced to metal sponge in the same general way; hafnium sponge being further purified by the iodide-dissociation method. The metallurgical development of hafnium about paralleled that of zirconium.

Hafnium has not been available in quantities to allow all of its potential uses to be determined, because all of the commercial output has gone to the account of the Government for use in nuclear reactors. The metal's high-melting point (2,150° C), high emissivity, and high specific gravity are coupled with excellent corrosion resistance. Hafnium's high-melting point and electron emission suggest uses in radio tubes and as rectifiers and cathodes for X-ray tubes. The oxide and carbide of hafnium are among the most refractory compounds with melting points of 2,664° C and 3,787° C, respectively. These compounds have received special attention recently because of the current interest in developing superrefractories for jet engines, nuclear reactors, and other high-temperature devices.

## PRODUCTION PROCESSES

The crystal bar or iodide process--the first commercial production method, now used mainly to purify or refine hafnium sponge--involves interaction of metal sponge or crude metal and iodine in a closed vessel and the subsequent thermal decomposition of the metal iodide. The container holding the crude zirconium and iodine is heated to about 400° C to volatilize the iodine which reacts to form zirconium iodide vapor. This gaseous compound decomposes upon contacting a filament (preferably of the metal to be reduced) which is heated to about 1,450° C. High-purity zirconium deposits on the heated filament, and the liberated iodine reacts with more of the sponge.

The magnesium-reduction or Kroll process, as it is widely known, consists of the following distinct steps: (1) reaction of zircon with carbon to form zirconium carbide, or zirconium carbonitride, (2) chlorination of this product to form crude zirconium-hafnium tetrachloride; (3) separation of the zirconium and hafnium by aqueous-solvent extraction--the resulting end products are zirconium and hafnium oxides, which are both processed to sponge in essentially the same manner; (4) the oxides are mixed with carbon, briquetted, and chlorinated (actually the zirconium-hafnium-separation step was not part of the process developed under Dr. Kroll's technical supervision); (5) the purified chloride is reduced with molten magnesium (a mixture of magnesium and sodium can be used); (6) the resulting sponge is purified by vacuum distillation; and (7) ingot is made by consumable arc melting purified sponge. Work done by the Bureau is summarized in one of its publications (6).

Production of commercial quantities of ductile zirconium and hafnium has been made possible by conducting the critical stages of the process in either a vacuum or in an inert atmosphere. The presence of oxygen, nitrogen, and hydrogen causes the metal to be hard and brittle. Exclusion of these common elements during reduction, therefore, is essential to successful operation of the process.

The Carborundum Metals Co. and Wah Chang Corp. use the magnesium-reduction process as developed at the Bureau of Mines. Carborundum Metals planned to add an electrolytic refining step to its hafnium production process (19). Hafnium sponge, made by the magnesium-reduction process, would be introduced into a molten salt bath as the anode. During the electrolytic refining step, hafnium metal would be deposited on the cathode. The purified metal then would be pressed into long electrodes and melted in a vacuum furnace. Use of this method would eliminate need for refining the metal by the more expensive iodide-dissociation (crystal bar) process.

A modification of the Kroll process is used by the Columbia-National Corp. In the initial step, zircon is fused with sodium hydroxide to form soluble sodium zirconate. This product is converted to zirconyl nitrate, and the hafnium is extracted with tributyl phosphate. The purified zirconyl nitrate is converted to oxide, chlorinated, and then reduced to sponge by the magnesium-reduction process. Chlorination is accomplished in a fluidized-bed reactor.

Bridgeport Brass Co. uses sodium in place of magnesium as a reductant. The company claims that liquid sodium is easier to handle than magnesium, that reductions made with it yield a purer metal, and that the cost of equipment for the initial installation is about 40 percent less when sodium is used. Instead of conventional sponge, the resulting metal is in the form of chunklets--formed by dripping molten zirconium on a revolving disc. These chunklets have the advantage of not being pyrophoric, but the last traces of sodium are difficult to remove, and they do not compress as readily as sponge when making consumable electrodes.

Bridgeport Brass has purchased overseas rights to a process for separating zirconium and hafnium (and subsequently reducing both to the metallic state) developed by the Commonwealth Scientific Industrial Research Organization of Australia. Reportedly, the separation step of the process is less costly than the solvent extraction method being used. Disproportionation, or preferential reduction of the zirconium to the less volatile trivalent state, makes separation from the quadrivalent hafnium possible. After the separation, the zirconium trichloride is heated to form tetrachloride, which then is reduced to metal with sodium.

A subsidiary of Kennecott Copper Co. (Kennecott Titanium Development Corp.) tested an electrolytic process licensed from Horizons Titanium Corp., Princeton, N.H. The company constructed a plant at Bedford, Ohio, to evaluate the process involving potassium zirconium fluoride in a fused sodium chloride bath.

## USES

### Brittle Metal

Impure zirconium metal is hard and brittle, and although it cannot be used as a structural material, it does have some other applications. In 1930, the metal came into favor as a smokeless flashlight powder for use in photography. Other uses employed its low-ignition point, rapid burning, and high heat of combustion. Commercial-grade ductile metal in sheet, wire, and powder form, now is being used for many applications requiring these properties.

### Ductile Metal

Low-hafnium, ductile zirconium (actually zirconium alloyed with varying amounts of tin as the main addition) is used by the Atomic Energy Commission and others in constructing nuclear reactors. The metal's corrosion resistance, strength at intermediate temperatures, and low rate of thermal neutron absorption have made it an important structural material in the field of atomic energy. Zirconium is used also for the jackets that contain the uranium-metal slugs in atomic-reactor cores and as a fuel moderator.

For nonnuclear applications, it is not necessary to separate the zirconium and hafnium. The resistance of zirconium to corrosion by alkalis and acids suggests important uses in the chemical industry for applications such as tank linings, pipes, valves, and immersion heaters. There is a good possibility that zirconium will replace the more expensive and heavier tantalum in

surgical applications. Zirconium is well suited for this use because of its high tensile strength and resistance to attack or discoloration by iodine, mercury salts, or high-temperature sterilization.

Zirconium can be used in steel to make certain high-strength parts and as a deoxidizer and scavenger to eliminate oxygen, nitrogen, and nonmetallic inclusions. Molten zirconium wets graphite, thus making possible direct metallic contacts between carbon and metallic parts as in rectifier tubes. The metal is used also to make metal-to-glass seals, such as would be required in glass-lined steel tanks. Sheet zirconium may find application in fluorescent lights because it is neutral to mercury and acts as a getter, thus extending the life of the tube indefinitely.

Zirconium-copper alloys (containing 33 and 50 percent zirconium) are of commercial interest. One percent of the master alloy added to copper raises the hardness "as cast" and the ultimate strength, and lowers the elongation. An alloy of copper-zirconium-cadmium has high strength and high conductivity, and is superior in strength and hardness to copper-cadmium alloys without severe loss of electrical conductivity.

The master zirconium-nickel alloys contain 50 to 75 percent zirconium. These alloys can be used in preparing high-speed cutting tools, for deoxidizing nonferrous alloys, and for degasifying nickel.

Magnesium-cerium-zirconium alloys have a combination of good casting qualities and good mechanical properties at ordinary and elevated temperatures, which makes them attractive for some important lightweight stress components of engines for which magnesium-base materials have been unsuitable in the past.

Zirconium is recommended for photoflash bulbs, when oxygen filled, because of its higher light output.

#### Nonmetallic

Zircon is used as an acid-type refractory; as an ingredient of high-temperature porcelain and as an opacifier in ceramic glazes and enamels; and as a foundry sand, abrasive, and insulating medium in manufacturing electrical heating appliances. Baddeleyite is used in manufacturing refractories, white-ware bodies, and glass-furnace linings. Glass-tank blocks are made of zircon; other blocks composed of zirconia (about 35 percent) and mullite, are used widely in the industry to combat abrasion at elevated temperatures.

The potentialities of zircon were recognized quite early by workers in the refractory field. The outstanding properties upon which refractory applications depend include: high melting and softening point--pyrometric cone equivalent (PCE) value approximately 42; thermal conductivity of an order similar to fire-clay but inferior to silicon carbide; relatively low thermal expansion; freedom from pronounced structural inversions; and satisfactory abrasion resistance and striking resistance to attack by certain molten metals, acidic chemicals, slags, and glasses. The original applications of zircon to the metallurgical industry were for brick, steel-ladle nozzles, crucibles, and cement for rammed monolithic linings.

Zircon probably is the highest temperature refractory (softening point about 2,531° C) in common use today that can be produced in bulk. It is very resistant to thermal shock and change of volume. In the aluminum industry, zircon refractories have been used successfully in building the working hearth in the reverberatory or open-hearth furnace which is used for melting, remelting, or alloying aluminum. Zircon refractories are preferred for this application over other superduty refractories because there is no penetration of the brick by metal, oxide, or vapor; no thermit reaction takes place with iron oxides and silica; and the refractory can take mechanical abuse when charging or cleaning the hearth and sidewalls. This refractory also has the peculiar property of not being wetted readily by aluminum metal or slag. Zircon is used also in glass-melting furnaces where very high temperatures are required.

For many years, zircon has found limited use as an ingredient of high-temperature porcelain because it imparts strength to the body and resistance to chemical action. The thermal endurance of zircon porcelain (45 to 60 percent zircon, balance clays and fluxes), especially for ultra-high frequency installations, is superior to steatitic porcelain.

The ceramic uses of zircon arise from its high reflectivity of light, high melting point and thermal stability, chemical inertness, and high specific gravity. A dual role is played by zircon in the formulation of glasses, glazes, and enamels; it is a low-cost source of soluble zirconia and is also an opacifier.

Since certain molten metals do not wet zircon, the mineral is used as a foundry and molding sand because grains of it will not adhere to the outer surface of the castings. Oil-bonded zircon sand is used as core material for special applications in foundry practice for gray iron, steel, some types of bronze, and light alloy castings. The thermal conductivity of zircon is much higher than that of silica sand commonly used in foundries; this is an advantage in constructing molds and cores, because the rapid chilling provided by zircon produces superior castings. Zircon flour is used as a core wash or paint which gives desirable results in stripping and finishing certain types of castings requiring exceptionally smooth surfaces. The wash makes the comparatively rough surface of the mold smooth as a result of the flour penetrating into the pores. Granular and flour zircon contain infinitesimal quantities of free silica; therefore, their use is not liable to give rise to silicosis. Table 12 compares certain properties of zircon, silica, and olivine.

Zirconia (chemically-prepared  $ZrO_2$ ), one of the most refractory of all substances, has a melting point of 2,695° C. It is relatively resistant to molten silicate slags and other corrosive materials, and is characterized by high strength, hardness, and resistance to abrasion. Zirconia has good high-temperature load resistance and can be used either in an oxidizing or reducing atmosphere. If not in direct contact with carbon, strongly reducing atmospheres are not harmful up to 2,000° C. Zirconia also is ordinarily unstable to thermal shock. Like the dioxides of silicon, titanium, and thorium, zirconia is polymorphic, and upon heating, goes through two inversions that are accompanied by volume changes as high as 7 percent and which result in mechanical failure of a zirconia body unless the transition temperature is

passed with extraordinary care. Addition of a few percent of a stabilizer results in the formation of a cubic configuration above 1,700° C that does not invert upon cooling, and the resulting body can withstand temperatures up to about 2,535° C.

TABLE 12. - Molding sand properties compared

Property	Silica	Zircon	Olivine
Color.....	White	Colorless to brown	Green
Specific gravity.....	2.28-2.33	4.4-4.8	3.2-3.6
Tap density.....lb per cu ft..	97	152-183	98-103
Rammed density:			
Clay-bonded, conventional.....do.....	<sup>1</sup> 97-104	<sup>1</sup> 156-173	<sup>1</sup> 102-110
Clay-bonded, twin peak.....do.....	<sup>1</sup> 113	-	<sup>1</sup> 118
Hardness.....Moh scale..	6.0-6.5	7.5	6.5-7.0
Melt point.....° F..	3110	4600	3400
Thermal expansion.....in. per in..	.018	.003	.0083
High-temperature reaction.....	Acid	Slightly acid	Basic

<sup>1</sup> Washington Iron Works Research by R. C. Hines, University of Washington, Seattle.

Source: Gould, H. E. Olivine in Ferrous Foundry. Foundry, October 1963, p. 86.

The high refractive index of zirconia plus its insolubility in silicate melts make it particularly suited for use as an opacifier in ceramic glazes and enamels; it is used alone or in conjunction with tin oxide. Zirconia is used as a component in a number of piezoelectric zirconates and appears to have some promise in semiconductor and fuel-cell applications. Fused stabilized zirconia also is used as an abrasive, particularly for polishing glass. The oxide also was used as a reflective-surface material on the satellite, "Explorer," sent into orbit in February 1958, and more recently, it found application as heat exchange pebbles for use at over 2,200° C for simulating reentry conditions in space research. Zirconia may find important applications in gas-cooled ceramic power reactors (9).

Zirconium boride has been reported to withstand temperatures as high as 3,316° C, and has been suggested as a suitable material for use in the combustion chambers of rockets and guided missiles. More recent examinations show that although the material has a very high heat conductivity, it also oxidizes very rapidly. For most applications, it would be necessary to coat the carbide with a dense film of zirconia to prevent rapid oxidation. Tests have proven that zirconia is better suited for jet nozzles and similar applications.

Soluble salts of zirconium, such as chlorides, sulphates, and acetates, are becoming more and more important commercially. Probably the largest consumption of soluble zirconium compounds is to render textiles water-repellent. Zirconium sulphate is used in leather tanning and may replace chromium oxide for this purpose. Zirconium chemicals are used as catalysts in organic syntheses and hydrocarbon cracking. These chemicals show particular promise as

radio-opaque substances for use in X-ray and fluoroscopic diagnosis. The citrate is used in metal replacement therapy to hasten removal of plutonium and radioactive yttrium from the body.

#### IMPORTS

The quantity and value of zircon imported into the United States from 1948 to 1963 are listed in table 13.

TABLE 13. - Zircon imports, 1948-63<sup>1</sup>

(Tons)

Year	Australia	Brazil	Canada <sup>2</sup>	Republic of South Africa	India	United Kingdom	Nigeria	Total	Value
1948	<sup>3</sup> 13,873	3,553	2	-	279	-	-	17,707	<sup>4</sup> \$571,161
1949	<sup>3</sup> 14,623	1,994	-	-	-	-	-	16,617	<sup>4</sup> 636,529
1950	<sup>3</sup> 15,098	697	141	-	-	-	-	15,936	<sup>4</sup> 431,107
1951	<sup>3</sup> 24,577	2,084	-	-	-	-	-	26,661	<sup>4</sup> 664,428
1952	<sup>3</sup> 21,500	1,972	-	-	-	-	-	23,472	<sup>4</sup> 630,559
1953	<sup>3</sup> 22,200	1,206	-	-	-	-	-	23,406	<sup>4</sup> 571,783
1954	<sup>3</sup> 16,300	1,408	-	-	-	-	-	17,708	<sup>4</sup> 486,555
1955	27,542	1,549	-	-	-	-	-	29,091	813,448
1956	30,351	331	303	-	-	155	-	31,140	791,612
1957	41,659	-	14	-	-	19	-	41,692	1,142,472
1958	19,175	-	-	-	-	-	50	19,225	467,391
1959	53,650	-	24	280	-	56	868	54,878	1,517,485
1960	29,183	-	2	3,133	-	112	1,850	34,280	1,233,815
1961	31,255	4	-	2,576	-	-	-	33,805	873,376
1962	27,001	-	1	3,326	-	-	544	30,872	844,939
1963	50,004	-	24	1,523	-	-	981	52,543	1,715,878

<sup>1</sup> 1963 total includes 11 tons from Austria.

<sup>2</sup> Probably country of shipment rather than origin.

<sup>3</sup> Approximate zircon in mixed rutile-ilmenite-zircon concentrates.

<sup>4</sup> Also includes value of the following quantities of rutile-ilmenite material:

1948--447 tons; 1949--4,216 tons; 1950--890 tons; 1951--631 tons;  
1952--435 tons; 1953--1,261 tons; 1954--949 tons.

Several hundred pounds of high-purity zirconium metal (believed to be recycled sponge) have been imported from Canada and the United Kingdom. Japanese producers shipped to this country about 165 tons of reactor-grade zirconium sponge valued at \$3.1 million during 1957-59.

#### CONSUMPTION

The apparent national consumption of zircon in 1962 was 89,000 tons, more than three and one-half times the quantity used in 1948. (See table 14). Average apparent consumption for the same period, by major categories, was ceramic and foundry uses, 48 percent; refractories, 26 percent; metals and alloys, 11 percent; and miscellaneous, 15 percent. Comparable figures are not available for the west coast.

TABLE 14. - Approximate U.S. consumption of zircon, 1948-62

Year	Short tons	Year	Short tons
1948.....	25,000	1956.....	58,000
1949.....	20,000	1957.....	85,000
1950.....	-	1958.....	54,000
1951.....	25,000	1959.....	81,500
1952.....	40,000	1960.....	89,000
1953.....	45,000	1961.....	92,100
1954.....	42,000	1962.....	89,000
1955.....	58,000	1963.....	<sup>1</sup> 37,500

<sup>1</sup> Excludes that quantity used at foundries.

#### Projection of National Zircon Consumption

A lack of available data narrowed the choice of variables for projecting national zircon consumption to time and gross national product (GNP). It is felt that both of these variables are good indicators of the movement and momentum of the economy, and by using each independently, a range of national zircon consumption through 1985 can be determined that seems to be plausible. (See fig. 8). The national and regional projections (figs. 8 and 9) were determined by employing least squares, linear-regression techniques.

The formula for the lower boundary is:

$$Y = 15.8106 + 5.7199X$$

$$R^2 = 0.88 \text{ (coefficient of determination).}$$

where

$$X = \text{time (1948 = 0)}$$

$$Y = \text{national zircon consumption (100 tons).}$$

The formula for the upper boundary is:

$$Y = -124.3556 + .4725X$$

$$R^2 = 0.88 \text{ (coefficient of determination)}$$

where

$$X = \text{GNP}^5$$

$$Y = \text{national zircon consumption (100 tons).}$$

Each  $R^2$  is significant at the 1-percent level using Student's "t" test.

Five marketing areas--Seattle and Spokane, Wash.; Portland, Oreg.; and San Francisco and Los Angeles, Calif.--were considered in this study.

No accurate measure of the quantity of granular zircon consumed on the west coast could be made; however, estimates by knowledgeable representatives of the industry indicate a range of 4,350 to 5,200 tons per year. Total

<sup>5</sup> Billions of 1954 dollars; GNP rate of growth = 4.1 percent as used in the Bonneville Power Administration's economic base study of the Columbia Basin.

imports of zircon into west coast ports for the years 1958 through 1962 average 5,106 tons. See table 15 for west coast imports of zircon, zirconium metal, and zirconium alloys. The 1963 increase in zircon imports to west coast ports, according to an informed industry source, was due mainly to the accumulation of large stocks by certain dealers. This stockpiling is not expected to be repeated in 1964; imports should approximate the 1962 totals. Since movement of the product after it passes through Customs cannot be traced readily, it must be assumed that the bulk of it remains in the area and that imports or supply are roughly equivalent to consumption.

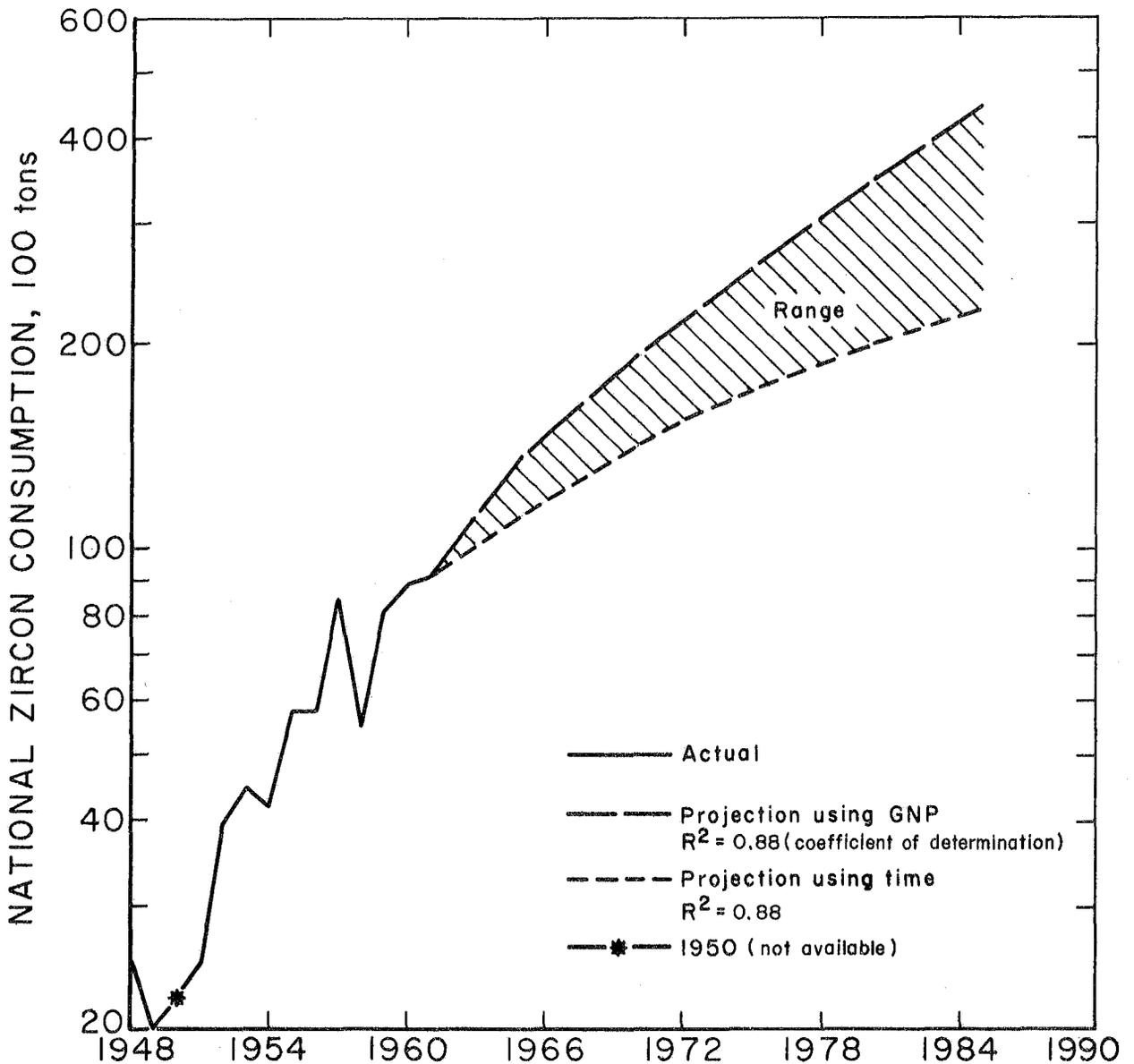


FIGURE 8. - National Zircon Consumption Actual and Projected, 1948-85.

TABLE 15. - West Coast imports of zircon and zirconium metal

Customs district	1949, zircon	1950, zircon	1951, zircon	1952, zircon	1953, zircon	1954, zircon	1955, zircon	1956, zircon
<b>Los Angeles:</b>								
Quantity.....pounds	8,900	257,800	541,108	417,882	2,229,381	1,372,026	3,352,122	{ 7,956,797 299,800
Value.....	\$74	2,423	6,118	4,791	26,893	17,664	55,153	{ 78,123 24,254
Country of origin.....	Australia	{ Australia Un. Kingdom						
<b>San Francisco:</b>								
Quantity.....pounds	18,000	231,724	385,636	526,674	881,846	556,898	477,120	{ 917,785 10,146
Value.....	\$309	2,172	3,733	5,961	9,438	6,313	5,063	{ 13,111 334
Country of origin.....	Australia	{ Australia Un. Kingdom						
<b>Portland:</b>								
Quantity.....pounds	-	-	-	100,800	199,360	-	224,013	936,363
Value.....	-	-	-	1,002	2,255	-	2,881	10,679
Country of origin.....	-	-	-	Australia	Australia	-	Australia	Australia
<b>Seattle:</b>								
Quantity.....pounds	-	-	-	100,016	799,680	-	364,963	{ 616,150 5,600
Value.....	-	-	-	\$1,738	9,045	-	4,292	{ 7,857 290
Country of origin.....	-	-	-	Australia	Australia	-	Australia	{ Australia Canada
<b>Total:</b>								
Quantity.....pounds	26,900	489,524	926,744	1,145,372	4,110,267	1,928,924	4,418,218	10,742,641
Value.....	\$383	4,595	9,851	13,492	47,631	23,977	67,389	134,648

TABLE 15. - West Coast imports of zircon and zirconium metal--Continued

Customs district	1957		1958		1959		
	Zircon	Zirconium	Zircon	Zirconium	Zircon	Zirconium	Zr alloy
Los Angeles:							
Quantity.....pounds	{ 4,955,801 33,600	-	1,778,549	222,000	4,723,766	6,000	2,240
Value.....	64,892 1,076	-	21,935	1,915,905	66,214	39,134	262
Country of origin.....	Australia Un. Kingdom	-	Australia	Japan	Australia	Japan	Japan
San Francisco:							
Quantity.....pounds	1,724,818	-	842,362	12,000	823,493	-	-
Value.....	22,973	-	10,101	79,431	9,175	-	-
Country of origin.....	Australia	-	Australia	Japan	Australia	-	-
Portland:							
Quantity.....pounds	448,000	-	4,319,726	47	3,315,776	-	-
Value.....	6,653	-	54,867	530	41,958	-	-
Country of origin.....	Australia	-	Australia	Japan	Australia	-	-
Seattle:							
Quantity.....pounds	280,000	2,376	449,479	2,062	183,152	-	-
Value.....	3,823	26,617	6,204	23,163	3,625	-	-
Country of origin.....	Australia	Japan	Australia	Japan	Australia	-	-
Total:							
Quantity.....pounds	7,442,219	2,376	7,390,116	236,109	9,046,187	6,000	2,240
Value.....	99,417	26,617	93,107	2,019,029	120,972	39,134	262

TABLE 15. - West Coast imports of zircon and zirconium metal--Continued

Customs district	1960		1961 Zircon	1962 Zircon	1963 Zircon
	Zircon	Zirconium			
Los Angeles:					
Quantity.....pounds	5,385,709	2,240	6,061,008	6,005,304	6,336,000
Value.....	107,340	8,700	73,321	77,396	( <sup>1</sup> )
Country of origin.....	Australia	Canada	Australia	Australia	Australia
San Francisco:					
Quantity.....pounds	854,363	-	2,328,142	1,790,493	2,374,000
Value.....	9,465	-	29,581	25,172	( <sup>1</sup> )
Country of origin.....	Australia	-	Australia	Australia	Australia
Portland:					
Quantity.....pounds	5,248,996	-	2,957,627	{ 3,176,927 302,400	10,104,000
Value.....	89,608	-	52,781	{ 40,581 4,201	( <sup>1</sup> )
Country of origin.....	Australia	-	Australia	Australia Un.S.Africa	Australia
Seattle:					
Quantity.....pounds	111,729	-	200,380	{ 99,022 100,800	1,508,000
Value.....	1,589	-	2,558	{ 1,184 1,383	( <sup>1</sup> )
Country of origin.....	Australia	-	Australia	Australia Un.S.Africa	( <sup>1</sup> )
Total:					
Quantity.....pounds	11,600,797	2,240	11,547,157	11,474,946	20,322,000
Value.....	208,002	8,700	158,241	149,927	<sup>2</sup> 331,757

<sup>1</sup> Not available.

<sup>2</sup> Estimate.

The quantity of zircon flour used as a foundry wash has been estimated by the same industry representatives to approximate 400 tons per year. No figures could be obtained which would substantiate the estimate. Apparently much of the milled zircon used for this purpose is imported, but the quantity cannot be determined because it is classified by Customs in a miscellaneous category of "earthy or mineral substance" and is not separable. Finely milled zircon used in the ceramic industry for the most part is shipped from eastern and midwestern concerns, but the quantities cannot be divulged without indicating sales of individual companies. High-quality milled zircon from Japan is being offered for sale in the Los Angeles area at two cents per pound below the domestic market price.

As far as can be determined, only one company on the west coast produces zircon or zirconia refractories (a small quantity made under license agreement to an eastern concern). Small quantities of zirconia kiln furniture are used. The main market, however, is for cast zirconia for lining and as feeders for glass-making furnaces. Some zircon refractories are used for tapping blocks in aluminum melting furnaces. Again there can be no disclosure of quantities shipped into the area for consumption. A small amount of zircon ramming mix is used for lining high-frequency furnaces.

Table 16 lists potential west coast zircon-products-consuming plants.

TABLE 16. - Potential west coast zircon-products-consuming plants

Industry	Washington		Oregon		California	
	Seattle	Spokane	Portland	Other	San Francisco	Los Angeles
<b>Glass:</b>						
Container.....	1	-	1	-	5	8
Pressed and blown.	-	-	-	-	1	6
Flat.....	-	-	-	-	-	1
Specialty.....	1	-	-	-	-	-
Ceramic tile.....	-	-	-	-	4	16
Vitreous sanitary ware.....	-	-	-	-	1	5
Vitreous china food utensils.....	-	-	-	-	2	7
Electrical porcelain	-	-	-	-	-	3
<b>Foundries:</b>						
Iron.....	<sup>1</sup> 18	-	8	<sup>2</sup> 5	39	47
Steel.....	9	2	6	-	9	25
Aluminum.....	4	3	8	<sup>3</sup> 1	21	129

<sup>1</sup> Western Washington.

<sup>2</sup> Linn, Lane, Coos, Josephine, and Baker Counties.

<sup>3</sup> Lane County.

Industry Comments by Area

## Seattle

Silica sand from out-of-State sources is used most commonly by foundries for molding purposes. Granular zircon is being replaced by olivine in most foundries that employ "special" sands. Reasons given for the substitution include: lower cost of olivine sand (less than half of the \$65 per ton charged for zircon) and the better service (functionability) of olivine. These factors apparently offset the higher binder requirements of olivine. Some imported zircon has an oil film that causes trouble with certain binders.

Milled zircon (flour) is used as a core wash. A small quantity is made in Seattle, but most of the supply comes from the Midwest. A zircon wash is not compatible with an olivine mold because zircon behaves as an acid refractory, and olivine is highly basic. Consequently, it has been predicted that olivine also will replace zircon as a wash material.

The only significant use of pressed zircon brick and cast zirconia (fused zirconia-alumina-silica) is for the bottoms, sidewalls, and feeders of glass-melting furnaces. A representative of the industry estimated consumption between 45 and 50 tons annually and thought that there might be a 10-percent increase by 1969. The tapping block of some aluminum-melting furnaces often is made of zircon. There apparently is very little use, if any, of other zircon-base refractories in the Seattle area.

## Spokane

A small quantity of granular zircon and flour is used by the foundry trade. Again, silica sand is the predominant molding material. One operator felt the need for a molding sand that would be better than silica--he had heard of zircon and olivine but had not tried either. Others stated that the "special" sands were too expensive, and that most customers would not pay a premium for a small benefit such as a smoother or cleaner casting surface.

Zircon blocks are used to some extent in the aluminum melting furnaces of companies making castings of that metal. No other utilization of zircon or zirconia refractories was indicated.

## Portland

Although silica is the predominant molding sand in general use in Portland, the city is the site of the foundry that consumes the largest quantity of granular and milled zircon on the west coast. Some foundries are using olivine in place of zircon, particularly when pouring castings of manganese steel.

Zircon refractories are being utilized in the manufacture of container glass and at plants producing aluminum castings.

### San Francisco (Northern California)

Most of the foundries in the area use silica sand for molding purposes. Some use zircon and olivine; however, substitution by olivine did not seem to be as common as in Oregon and Washington. Some of the milled zircon requirement is imported; the balance is shipped from the Midwest.

Zircon brick and cast zirconia-alumina silica block are used by companies making glass and aluminum castings. A small quantity of crucibles, covers, and kiln furniture is marketed in the area.

Ceramic-grade zirconia is used to some extent in glazes and enamels by concerns making ceramic tile and vitreous sanitary ware and china food utensils.

### Los Angeles (Southern California)

The situation regarding foundry sands and washes, for the most part, parallels that found in the other areas under study. Replacement of zircon by olivine, however, seems to be more prevalent than in the San Francisco area.

Zircon and zirconia in their various forms for ceramic and refractory purposes are utilized to some extent by many of the firms making aluminum castings, glass, ceramic tile, sanitary ware, vitreous china, and electrical porcelain. Crucibles, combustion boats, covers, and shields find rather widespread use in the area.

One company makes a small quantity of zircon refractories--mainly zircon ramming mix--under contract to an eastern manufacturer.

Concern was expressed over the impact Japanese imports of sanitary ware were having upon the local industry. It is feared that, as a result of these imports, the sanitary-ware industry might decline to the depressed condition of the artistic-pottery industry. Imports almost made the artistic-pottery industry extinct in California.

### Projection of West Coast Zircon Imports (Consumption)

There is reason to believe that the economic development of mineral commodities, like many biological phenomena, follow certain mathematical formulae called growth curves. There are many types of growth curves ranging from those of simple harmonic motion

$$Y = K + A \sin \frac{2\pi t}{P} + B \cos \frac{2\pi t}{P} ,$$

to those of constant percentage change such as the logarithmic straight line,

$$Y = AX^b .$$

Knowledge of the commodity and its history are necessary to select the proper type of curve to use.

The use of zircon on the west coast developed slowly but steadily. According to available records, the first imports were received in 1949. As the desirable properties of the mineral became more widely known, it was used to replace less suitable materials, and new markets came into existence. Zircon maintained its favorable position until the introduction of olivine as a competing raw material for certain applications. At this point, the growth rate of zircon began to slacken. The Gompertz growth curve was selected as the best means of illustrating this situation. It is felt that a better fit of the data was obtained than would have been the case had a strictly linear or curvilinear interpretation been used.

$$Y = AB^C X$$

Using west coast import data for 1948-62 (1963 figures were not included because of stockpiling by dealers), the following formula was developed for projecting consumption of zircon:

$$Y = 5990 (.0003613)^{.72155^X},$$

$$\text{or } \log Y = 3.7742 - (3.44218) \cdot 72155^X$$

$$R^2 = 0.86$$

where

Y = west coast zircon imports (tons)

X = time (1948 = 0)

The  $R^2$  is significant at the 1-percent level using Student's "t" test.

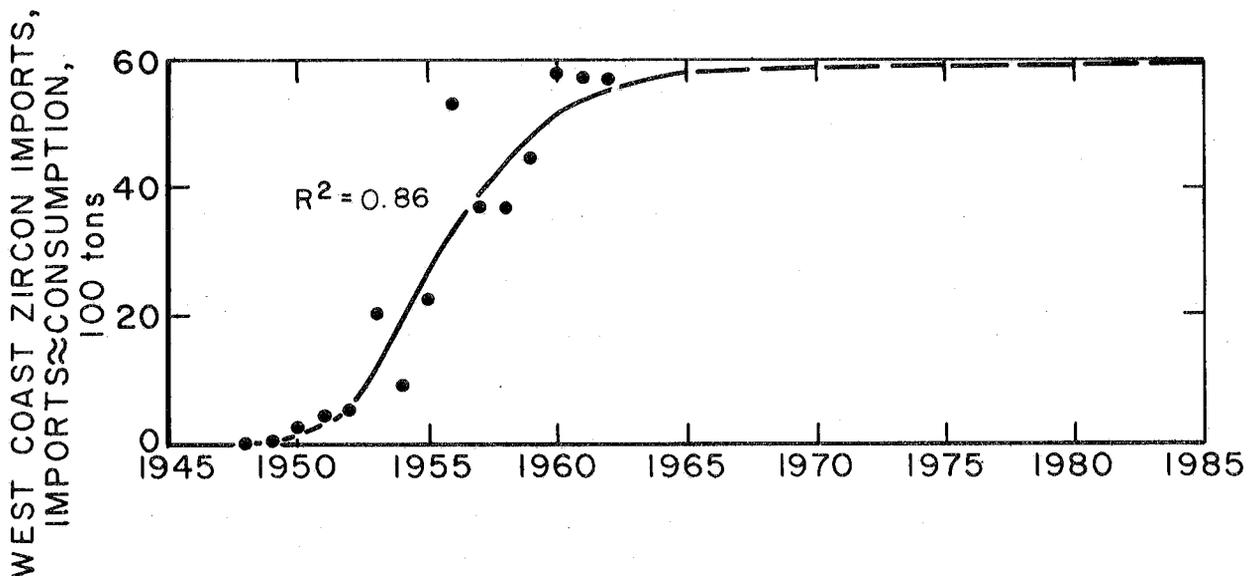


FIGURE 9. - West Coast Zircon Consumption Actual and Projected, 1948-85.

Figure 9 shows that west coast zircon consumption is not expected to decrease. While it is conceded that olivine has replaced zircon to a large extent as a foundry sand, growth in other uses will allow zircon to maintain its present position or, possibly, to increase slightly. The possibility always exists, of course, that unforeseen forces may alter the future growth rate pattern substantially.

#### EXPORTS

Exports of zircon ore and concentrates, and zirconium metal and alloys (crude, scrap, and semifabricated forms) are listed in table 17.

Most of the ore and concentrate shipments have been to Canada and Mexico. Canada and the United Kingdom are the principal recipients of the exported metal.

TABLE 17. - United States exports of zircon ore and concentrates  
(primarily milled) and zirconium metal

Year	Zircon		Form	Zirconium	
	Quantity (tons)	Value		Quantity (pounds)	Value
1948	312	\$24,137	Zirconium metal and alloys.....	21,966	\$7,911
1949	305	23,654	.....do.....	74,991	12,942
1950	-	-		-	-
1951	370	36,548	Zirconium metal and alloys.....	83,461	49,675
1952	584	42,221	.....do.....	51,151	42,677
1953	1,100	89,183	{ Zirconium metal and alloys--crude and scrap	6,600	7,047
			{ Semifabricated forms.....	145	1,729
1954	692	42,725	{ Zirconium metal and alloys--crude and scrap	39,678	5,254
			{ Semifabricated forms.....	2	593
1955	779	58,480	{ Zirconium metal and alloys--crude and scrap	105,600	61,746
			{ Semifabricated forms.....	1,132	39,007
1956	1,048	90,011	{ Zirconium metal and alloys--crude and scrap	18,519	187,046
			{ Semifabricated forms.....	468	13,317
1957	3,160	315,378	{ Zirconium metal and alloys--crude and scrap	66,000	359,204
			{ Semifabricated forms.....	1,151	24,385
1958	1,994	336,470	{ Zirconium metal and alloys--crude and scrap	86,000	558,979
			{ Semifabricated forms.....	14,282	198,286
1959	1,511	262,772	{ Zirconium metal and alloys--crude and scrap	80,000	384,000
			{ Semifabricated forms.....	10,100	277,000
1960	1,382	316,663	{ Zirconium metal and alloys--crude and scrap	996,000	1,679,362
			{ Semifabricated forms.....	70,000	928,006
1961	1,277	278,244	{ Zirconium metal and alloys--crude and scrap	88,000	442,436
			{ Semifabricated forms.....	90,000	1,029,823
1962	1,666	365,184	{ Zirconium metal and alloys--crude and scrap	144,000	658,545
			{ Semifabricated forms.....	74,000	1,081,372
1963	1,418	304,881	{ Zirconium metal and alloys--crude and scrap	216,451	1,071,865
			{ Semifabricated forms.....	75,341	1,428,395

#### FREIGHT RATES

Tables 18 and 19 list rail rates and table 20 truck rates for zircon concentrates shipped from Boise, Idaho, to the various marketing areas under consideration. Most of the rates are "class rates" (cents per hundred-weight); only Portland has "commodity rates" (cents per ton). Very likely, commodity rates could be established for the other areas, if relatively large shipments were made on a sustained basis.

TABLE 18. - Railroad transportation rates for zircon ore  
(Cents per hundredweight)

Origin	Destination	Rate <sup>1</sup>	Minimum weight
Boise, Idaho.....	Spokane, Wash.....	186	Less than carload.
Do.....	...do.....	94	60,000 lbs.
Do.....	Seattle, Wash.....	207	Less than carload.
Do.....	...do.....	104	60,000 lbs.
Do.....	Portland, Oreg.....	191	Less than carload.
Do.....	...do.....	96	60,000 lbs.
Do.....	Albany, Oreg.....	207	Less than carload.
Do.....	...do.....	104	60,000 lbs.
Do.....	San Francisco, Calif.....	276	Less than carload.
Do.....	...do.....	139	60,000 lbs.
Do.....	Los Angeles, Calif.....	330	Less than carload.
Do.....	...do.....	166	60,000 lbs.

<sup>1</sup> Class rate.

Source: General Services Administration, Transportation and Communications Service, Auburn, Wash.

TABLE 19. - Railroad transportation rates for zircon ore  
(Cents per ton)

Origin	Destination	Released value per ton	Rate <sup>1</sup>	Minimum weight
Boise, Idaho.....	Portland, Oreg.....	\$0 to \$20	728	100,000 lbs.
		20 to 30	816	
		30 to 40	905	

<sup>1</sup> Commodity rate.

Source: General Services Administration, Transportation and Communications Service, Auburn, Wash.

TABLE 20. - Truck transportation rates for zircon ore  
(Cents per hundredweight)

Origin	Destination	Rate	Minimum weight
Boise, Idaho.....	Spokane, Wash.....	204	Less than truckload.
Do.....	...do.....	143	60,000 lbs.
Do.....	Seattle, Wash.....	222	Less than truckload.
Do.....	...do.....	155	60,000 lbs.
Do.....	Portland, Oreg.....	191	Less than truckload.
Do.....	...do.....	96	60,000 lbs.
Do.....	Albany, Oreg.....	311	Less than truckload.
Do.....	...do.....	208	60,000 lbs.
Do.....	San Francisco, Calif.....	300	Less than truckload.
Do.....	...do.....	210	60,000 lbs.
Do.....	Los Angeles, Calif.....	376	Less than truckload.
Do.....	...do.....	263	60,000 lbs.

Source: General Services Administration, Transportation and Communications Service, Auburn, Wash.

A blanket rate of \$42.65 per net ton has been established for shipping Florida zircon by rail to west coast destinations. About 98 percent of the transcontinental shipments are by rail; the balance, usually in quantities of less than one ton, are by truck. Nigerian zircon was shipped by rail from Houston, Tex., to Albany for \$42.50 per ton.

Ocean freight for Australian zircon brought into west coast ports is about \$24 per ton. Delivered price for the concentrate in Albany is \$54, including a \$5 handling charge from Portland. The ocean freight for zircon from the Union of South Africa delivered in Seattle is about \$20 per ton. Australian zircon sells in Seattle for \$65 per ton and in Los Angeles for \$60 per ton.

### PRICES

The price of Australian zircon, c.i.f. Atlantic ports, has varied somewhat over the past 15 years. It was lowest in 1953, \$42 to \$43, and highest in 1951, \$47 to \$72. Since April 1959, the price has held steady at \$50 per long ton. Domestic zircon has been quoted at \$47.25 per short ton f.o.b. Starke, Fla., for the past several years.

In 1948, before any sizable quantity of zirconium had been made by the magnesium-reduction process, crystal-bar zirconium was quoted at \$300 per pound. The price dropped to \$90 by 1951, and to \$70, for quantities in excess of 100 pounds, the following year where it remained through 1956. There have been no recent quotations.

Zirconium made by the magnesium-reduction process was valued at about \$100 per pound in 1948. In 1951 it was offered at \$10 per pound. In 1955, reactor-grade sponge ranged from \$10 to \$14 per pound, and 500-pound ingots were offered at \$23.07 per pound. Commercial-grade ingots of the same size were quoted at \$14.40 per pound. Two years later, reactor-grade sponge was \$7.50 to \$10 per pound, and commercial-grade was \$5 to \$7. Reactor- and commercial-grade ingots ranged from \$10.50 to \$12.50 and \$7.75 to \$9.75 per pound, respectively. The quoted price of reactor- and commercial-grade platelets set at \$7 to \$14 and \$5 to \$10, respectively, in 1957 has not changed. Reactor-grade sponge has held steady at \$6.25 per pound for small lots since 1958. The price ranges downward to \$4.50 for larger quantities.

Gram lots of high-purity hafnium metal powder were offered for about \$22 from 1952 to 1956. After the zirconium-hafnium separation step had been adapted commercially, hafnium sponge was furnished to the AEC under contract for \$13 per pound. There was an additional charge of \$13.50 a pound for the iodide "refining" step required to bring the metal to specification grade. A short ton of Australian zircon contains about \$6,000 worth of zirconium and hafnium at current AEC prices. If the 20 pounds of contained hafnium was to bear the entire cost, the purified zirconia probably would not be reduced to sponge, and the hafnium would cost about \$250 per pound.

From prices listed in this section and from the freight-rate data in the preceding section, it appears that domestic (Florida) zircon delivered by rail

to west coast destinations would cost \$89.90 per short ton, and Australian zircon shipped the same way from Eastern United States would cost \$97.71 per long ton. The price of Australian zircon imported directly to west coast ports ranges from about \$54 to \$65 per long ton.

## OUTLOOK

### National

There should be no shortage of zircon nationally in the foreseeable future. An established industry in Florida capable of expanding its production, coupled with imports from Australia, substantiates that observation.

Because Government use has accounted for most of the reactor-grade zirconium (and hafnium) produced during the relatively short span of years since development of the magnesium-reduction process, the normal relationship between price and supply and demand has not had a chance to develop in the usual economic sense. However, zirconium's properties have made it extremely desirable as a structural material in nuclear reactors, as well as a fuel-cladding material and as a moderator. Stainless steel, its closest substitute, has somewhat similar corrosion-resistant properties and a relatively low capture cross section (although it is about 15 times greater than zirconium). The downward trend in the price of zirconium has played an important role in helping the metal maintain its position relative to stainless steel. Further reductions in price almost necessarily must be made, if this situation is to continue.

Contracts for producing reactor-grade zirconium (referred to in another section) have terminated. Therefore the effect this will have upon the future demand for zirconium metal must be considered. Statistical procedures as an aid in determining the probable future market growth of the industry cannot be applied to an infant industry such as this. Demand for zirconium metal cannot be correlated usefully with such economic indicators as gross national product or the Federal Reserve Board indexes of industrial production.

Future of the zirconium-metal industry would seem to depend upon (1) continued use of zirconium and hafnium in nuclear reactors, (2) expanded use of commercial-grade zirconium, and/or (3) development of new large-scale applications not presently envisioned. Although sufficient data were not available which would allow calculation of trends that could lead to projections, market research to obtain the opinions of those closest to the industry could be employed. Inquiries regarding the future of zirconium for both reactor and commercial uses were directed to the Atomic Energy Commission; Zirconium Association; Wah Chang Corp.; Columbia-National Corp.; Bridgeport Brass Co.; The Carborundum Metals Co.; and Harvey Aluminum, Inc.

The following sections reflect the considered opinions of representatives of these organizations:

The major problem confronting the zirconium industry at present is the sharp drop in demand for the metal resulting from termination of Government-purchase agreements. The contracts to furnish 5,500 tons of reactor-grade

metal, over a 5-year period, have expired. Industry, at least for the immediate future, must cope with the problem of imbalance between diminished demand and production capabilities. Requirements probably will be less than half of the 2-million pound annual output reached by the time the contracts ended in 1961. This, of course, will place the industry in a precarious position.

The long-range outlook for new reactor cores and for replacement cores, as viewed by those contacted, seems good. It is felt that the commercial use of zirconium and hafnium in pressurized water and boiling water reactors will dominate for 10 to 20 years. Still looking ahead--the timing of such a program, the time lag before this new industry develops to the stage of requiring substantial quantities of these metals, may be as far as 5 years away. Continued use of zirconium for structural and cladding purposes in naval underwater craft is anticipated. It is expected that more naval surface ships and ultimately commercial vessels will be nuclear powered. Another important consideration is that other free world countries are becoming increasingly interested in the use of zirconium and hafnium for nuclear applications. The high cost of conventional power in some of these countries may provide the impetus to launch nuclear-power development. It also is believed that the few producing companies in these countries are not attempting to scale-up production for such an eventuality, nor do they plan to do so.

The four primary producers of zirconium are faced with an immediate and serious situation--the need for a drastic reduction in production. Indications are that the AEC program will continue at the level of the past several years. This will require about one million pounds of zirconium yearly, roughly half of the average annual output during the period of the contracts just terminated. It also appears that approximately 50 percent of the output in recent years has swelled the Commission's inventory. If this is so, stocks on hand should be equivalent to about 2-year's production. Because of the possible effects on the industry, it would be contrary to the best interests of the AEC and the national defense program to exhaust this inventory before negotiating for additional supplies. Industry, of course, would like to maintain the operational level of the past 5 years, but it cannot do this without a market. A plan attributed to the AEC is to deplete its inventory by 500,000 pounds per year and to purchase an equivalent quantity over a 5-year period. Industry feels that its chances of survival would be better, if the inventory were reduced by a smaller amount each year. It should be mentioned at this time that the apparent surplus of zirconium over the anticipated requirements estimated for the past several years has been attributed mainly to longer life of nuclear cores, newer cores requiring smaller quantities of zirconium per unit of power produced, and improved techniques for recovering and utilizing scrap.

Since the future of the zirconium industry will depend to a large extent upon Government programs, it may be well to outline briefly some current planning as presented in an AEC report (36). The position maintained by the Commission was reiterated in a report to the President on November 20, 1962 "--recommended that the Government provide economic incentives to private and public utilities to bring the already-developed water-cooled types of reactors into more widespread use---."

To date, there are 11 civilian reactors that are Government owned, 12 that the Government and a utility company share expenses, and 7 that have been initiated by public utilities using Government technology. These reactors are considered experimental or developmental rather than the larger production types. As of December 31, 1962, the status of the civilian prototypes of large central-station plants was 6 operable, 5 under construction, and 3 planned. One of those under construction is at Humboldt Bay, Calif., and two of those planned also will be in California--at Camp Pendleton and at Bodega Bay.

A possible power-reactor program for the next 12 years according to the report might entail--

1. Constructing and placing in operation 7 or 8 power-producing prototype reactors, approximately half of which would be advanced converters and the rest breeders; most of the cost will be borne by the AEC.
2. Assisting, as necessary, industry in constructing 10 or 12 full-scale powerplants of improving design as time goes on; industry will concurrently bear full costs of many more of well proven design.

The report further indicated that the authorized level of our naval nuclear fleet was 3 destroyer leaders, 1 aircraft carrier, 1 cruiser, and 75 submarines. At the end of 1962, the Enterprise (aircraft carrier), the Long Beach (cruiser), the Bainbridge (destroyer), and 28 submarines had been commissioned.

Major objectives of the naval reactor program are--

1. Development of advanced nuclear propulsion plants ranging in size and power ratings from plants in small submarines to reactor plants for larger surface ships.
2. Development of improved reactor cores and components with significantly longer lifetimes which will result in fewer refuelings, lower fuel costs, and less out-of-service time for naval ships.

Industry expects a stronger market to develop for commercial-grade metal, although at a slow rate. There should be a gradual increase in the use of zirconium in the chemical industry. Such use would be predicated upon the metal's outstanding corrosion-resisting properties. Acceptance is slow because of the time involved in evaluating the resistance of the metal to various corrosive media, and because of the problems attending development of competent sources of supply for the various types of equipment required by the industry. Increasing interest is being shown in the superconductive and high-temperature alloys of zirconium; however, the quantity of the major metal employed would not be very significant.

Thus far in this section, the presentation seems to have assumed the position of protecting or maintaining the "status quo" of the four primary

zirconium producers. This was not necessarily the intent. While a worthwhile objective, it is not logical to believe that each of these companies can withstand up to 5 years of drastically curtailed production just in hopes of a brighter future. Based upon what is known at the present time, the major market for reactor-grade zirconium will be reduced to about 500,000 pounds per year for the next 5 years. It has been proposed that contracts for production of that quantity be issued to two or more of the primary producers on the basis of competitive bidding. This is not very encouraging when it is recognized that the entire quantity (500,000 pounds) represents no more than half of the annual capacity of the four producers. It is highly doubtful that each of the present producers will be able to continue its plant operation on an economical basis under the indicated conditions; however, it is not within the province of this study to speculate as to what the position of a relatively small but fully integrated producer of zirconium and hafnium would be compared with that of companies having broad organizational backing and maintaining much larger production facilities.

To summarize, the position of reactor-grade zirconium and hafnium will remain relatively unchanged. Its use as a structural and cladding material in propulsion-power plants as well as in electrical-power plants will continue at about the present level for the next 3 to 5 years. After that, assuming no major changes in technology which would introduce a more desirable metal or alloy or a radical change in the basic reactor, the use of zirconium can be expected to increase as larger powerplants and nuclear-powered surface ships are built.

Commercial zirconium should follow the same pattern but at a slower rate. The outlook for use of the metal and its alloys is especially bright in the chemical and marine industries. The need for a metal with superior corrosion-resistant properties in the chemical equipment industry is acknowledged. It has been estimated that corrosion damage in this industry alone totals \$5 million annually.

#### Regional

Development and utilization of western zircon resources, unless unexpected events transpire, seem remote at this time. Production of coproducts, including ilmenite, chromite, monazite, and columbium-tantalum minerals, while essential to an economic dredging operation in the area under consideration, unfortunately, will not provide a panacea.

Ilmenite occurs rather abundantly in many of the placers in the area. This would suggest that development of a titanium industry on the west coast would be reflected in exploitation of these deposits. According to a recent study (17), there exists the possibility that a titanium sponge-metal plant and a titanium dioxide pigment plant might be built in the Pacific Northwest by 1970. Availability of low-cost power would be the most important factor that would influence a decision to produce sponge in the region, while western consumption by the pulp and paper industry and by paint manufacturers would be the principal plant location factor for the establishment of the titanium dioxide pigment plant. The report indicated that a titanium dioxide pigment

plant was scheduled for earlier completion in California, with imported rutile, not ilmenite, to be used as the raw material. In the Pacific Northwest, according to the report, imported rutile would probably be used initially. Later, owing to increased demand and prices for rutile, producers might turn to domestic resources. On the optimistic side, an operation might be established to produce pig iron and high-titanium slag by electric-furnace smelting of ilmenite. The byproduct slag could be the raw material for making both the pigment and the sponge metal.

Chromite, the potential coproduct of zircon in Oregon sands, is low grade and is acceptable only under conditions of dire necessity.

Monazite and columbium-tantalum minerals have been produced from Idaho placers in recent years. If imports of monazite were curtailed, or if national needs required increased quantities of the mineral at any cost, production could be resumed. There exists a strong possibility that dredging for columbium-tantalum minerals in Bear Valley will be resumed. The low zircon content in this particular area, however, precludes recovery of significant tonnages of that mineral as a byproduct.

In California (63), known concentrations of zircon are considered to be too low in grade to recover commercially at present.

The only logical conclusion that can be drawn, under present conditions, is that there is very little likelihood that west coast zircon resources will be developed until the time that a substantial market exists for the more important coproducts.

West coast consumption of zircon cannot be measured with any degree of accuracy; therefore, it has to be assumed that the quantity used closely parallels imports. Receipts of zircon into west coast ports have increased from 13.5 tons in 1949 to 10,200 tons in 1963. Use of zircon as a foundry sand, the major nonmetallic application, has been decreasing steadily over the past 4 or 5 years, according to representatives of the industry. As was previously noted, there has been a steady increase in use of olivine for this same purpose, but the magnitude cannot be disclosed because of company-confidential data. If less zircon is being used by the foundry industry, other uses must be requiring greater quantities as indicated by the static condition of apparent consumption (imports) from 1960 through 1962, or possibly certain consumers are increasing their stocks. Since there are no indications that other nonmetallic applications are increasing, the use of zircon for making ductile zirconium metal during this period must have offset the drop in consumption by the foundry industry. Whether this condition will continue is problematical; however, zircon consumption on the west coast probably will remain at about the present level for the next 5 years; certainly, a significant increase would seem unlikely.

Although this study is concerned primarily with the west coast area, consideration of the future of the zirconium industry, thus far, has been national in scope. This is not unusual, for in many cases regional development of a commodity or industry depends upon the national situation. The

quantity of zircon used for making zirconium on the west coast is not very large, nor is the capacity of the plant at which it is made. These factors may be advantageous to the area; during a period that will witness national output of zirconium being reduced to less than half of the annual average for the past 4 or 5 years, a relatively small but fully integrated company may be in position to maintain its level of production. Representatives of the Wah Chang Corp. are very optimistic in their outlook. The company is in a favorable position competitively because of its fully-integrated operation and because commercial markets had to be developed when Government contracts terminated several years ago. An advantage of the integrated operation is the ability to recycle scrap of known composition. Harvey Aluminum, Inc., also is looking forward with confidence. The company has a large market for zirconium sheet, plate, forgings, and tubing in this country and abroad.

The feasibility of constructing a new zirconium reduction plant on the west coast was considered in the early stages of this study. Because of the position the industry finds itself in nationally, it is extremely unlikely that such a facility will be required or built in the foreseeable future. The reader who would be interested in the costs of operating a plant of this type is referred to an interesting study made recently on the economic feasibility of a zirconium reduction plant in northern California (64).

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