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MINERALOGY OF BLACK SANDS
AT
GRAYS HARBOR, WASHINGTON

By
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FOREWORD

Interest in Pacific Coast black sands as a possible source of mineral value dates back to before the turn of the century. In the early days the interest was mainly in gold and platinum that were contained in the sand in some localities. During World War II, Oregon black sands were mined and concentrated for their chromite content.

Since World War II a considerable amount of attention has been given to Washington black sands along the lower Columbia River and at Grays Harbor and other coastal areas. Most of this interest has been in the sand as a possible source of iron and titanium. Some interest has been shown also in some of the accessory heavy minerals in the sand. It has been thought that zircon and garnet, at least, might be recovered as byproducts of iron and (or) titanium production.

Small high-grade deposits of black sand and large accumulations of sand containing small amounts of heavy black minerals have been found in Washington, but to date no production has been recorded. The feasibility of mining and marketing Washington black sands would depend not only on the size and grade of the deposits but also on their mineralogy. Part of the problem has been the difficulty in producing high-grade iron and titanium concentrates, and this is largely a result of the mineral composition of the sands.

The investigations reported in this volume, "Mineralogy of Black Sands at Grays Harbor, Washington," were conducted to answer some of the questions as to the mineralogical content of the sands. The mineralogical data reported here should be helpful in any further investigations that may be made to determine the feasibility of mining the black sands in the Grays Harbor area.

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MINERALOGY OF BLACK SANDS
AT
GRAYS HARBOR, WASHINGTON

By Gerald W. Thorsen

ABSTRACT

Nine shallow sand samples were taken on the tidelands just inside the mouth of Grays Harbor, Washington. All but a small fraction of each sample was sent to a large mining company for beneficiation and Davis tube tests. Cuts from three samples were retained for sieve, heavy liquid, and magnetic separations. The richest one of these was examined by both transmitted- and reflected-light microscopes, and numerous spectrographic analyses were also made.

Studies of opaque polished grains having a specific gravity greater than 4.3 and various magnetic susceptibilities showed a wide variety of titanium-iron mineral intergrowths. Very little pure magnetite was found, but what appeared to be a titanium-rich (in solid solution) variety of magnetite was fairly abundant. Ilmenite was about equally abundant. Also present were many grains in which both magnetite and ilmenite occur together as intergrowths. Minor hematite was present in the most magnetic of the three magnetic splits. The proportion of hematite increased to form about two-thirds of the weakest magnetic concentrate, in which the only other mineral present in appreciable quantities was chromite. These three magnetic fractions together made up 12.5 percent of Sample No. 5.

Microscopic examination of the transparent minerals in No. 5 showed the following: zircon (0.7 percent), rutile (0.12 percent), garnet (5 percent); kyanite and staurolite were also present. Hypersthene makes up approximately 20 percent of the sample. Abundant magnetite inclusions caused the hypersthene to concentrate over a wide magnetic range.

INTRODUCTION

PURPOSE AND SCOPE

The purpose of this study was to determine what heavy minerals^{1/} are present in the Grays Harbor sands, and in what amounts and grain size ranges they occur. In answering these questions, sieve, heavy liquid, and magnetic separations were made on three of the nine samples taken in the field. Of these three the sample (No. 5) having the highest heavy mineral content was selected for mineral identification studies and grain counting of the +3.5 specific-gravity fractions. An attempt was made to produce the purest possible magnetite and ilmenite fractions without regard to what might or might not be economically recoverable on a commercial scale. The degree of success can be judged by examination of the analysis in table 2, on page 20. Polished sections and chemical analyses were made of the more magnetic fractions of this sample. Identifications and grain counts of both liberated grains and intergrowths were based on optical properties, hydrochloric acid etch reactions, specific gravity, and magnetic susceptibility.

In an attempt to get samples containing enough heavy minerals to work with conveniently, the richest known area was selected for sampling. This area (described on page 3) was the richest found by the United States Bureau of Mines in a reconnaissance of the ocean beaches in 1954 and 1955 (E. A. Magill, oral communication). The major North Bay tidelands lessees also considered this an area of placer concentration. Wind concentration of the heavy minerals by selective winnowing above normal high tide left lenses of "heavies" as much as several inches thick that contained little material lighter than garnet.

Samples from the 0 to 5-foot section of a hole drilled by the U. S. Bureau of Mines near the location from which Sample No. 5 was taken agreed

^{1/} Sedimentary petrologists usually define a "heavy mineral" as one heavier than bromoform (approximately 2.85 sp gr). Economic geologists often seem to imply something heavier, but rarely give a definition, and often compound the problem by introducing (again without defining) such terms as "semi-heavy mineral." In this paper a heavy mineral is defined as one heavier than 3.5 sp gr. This seems to be a logical choice, as few detrital minerals of commercial value are under 3.5 and few of the abundant rock-forming minerals are over this value. Where a more precise designation is needed, the specific gravity limits are stated.

to within about 2 percent of the TiO_2 content of Sample No. 5 (Dean Holt, written communication, June 26, 1959). In the following text the mineral percentages cited refer specifically to Sample No. 5 unless otherwise stated.

GEOGRAPHIC AND GEOLOGIC SETTING

Grays Harbor is a shallow bay on the coast of the State of Washington. The entrance channel from the Pacific Ocean passes between two low, partly wooded bay-mouth sandbars. The harbor extends eastward about 17 miles inland, and at its widest place its width is 14 miles. Its area at high tide is 94 square miles, and at low tide approximately 37, leaving about 57 square miles of tidelands. At points in the harbor more than 5 miles from the mouth, the bottom is generally of mud.

Precipitation in the area averages about 81 inches annually, and temperatures near the harbor mouth generally range from 41° to 59° . The prevailing winds are from the east in December, January, and February, and generally from the northwest and west during the rest of the year. High winds and storms usually come from the southwest. The prevailing longshore current at the mouth of the harbor flows to the north (University of Washington Department of Oceanography, 1955, p. 12-13, 78, 136, 138).

The area sampled is inside the Harbor at the southern tip of the large bay-mouth bar that separates North Bay from the Pacific Ocean. This area can be reached by traveling 20 miles of paved public road from Hoquiam to the settlement of Oyhut near the base of the north peninsula. From here one may travel south 5 miles by improved road over private land to the area sampled. The area is approximately 13 miles by road and $8\frac{1}{2}$ miles by water from the nearest existing rail facilities near the mouth of the Humptulips River.

The tidelands of Grays Harbor are State owned, and almost all the area has been leased to individuals for prospecting purposes. None of these prospecting leases have been converted to mining leases at this time (1962). Most of the individual lessees have assigned their leases to Mr. Willis G. Bunker, Hoquiam, Washington. In 1962 he controlled approximately 500 leases, comprising 40,000 acres of tidelands. Mr. Bunker and his associates also control a substantial acreage of land adjoining the bay that they plan to make available to any industry utilizing black sands.

The drainage tributary to Grays Harbor is composed largely of Tertiary sedimentary and volcanic rocks. The sedimentary rocks are both marine and non-

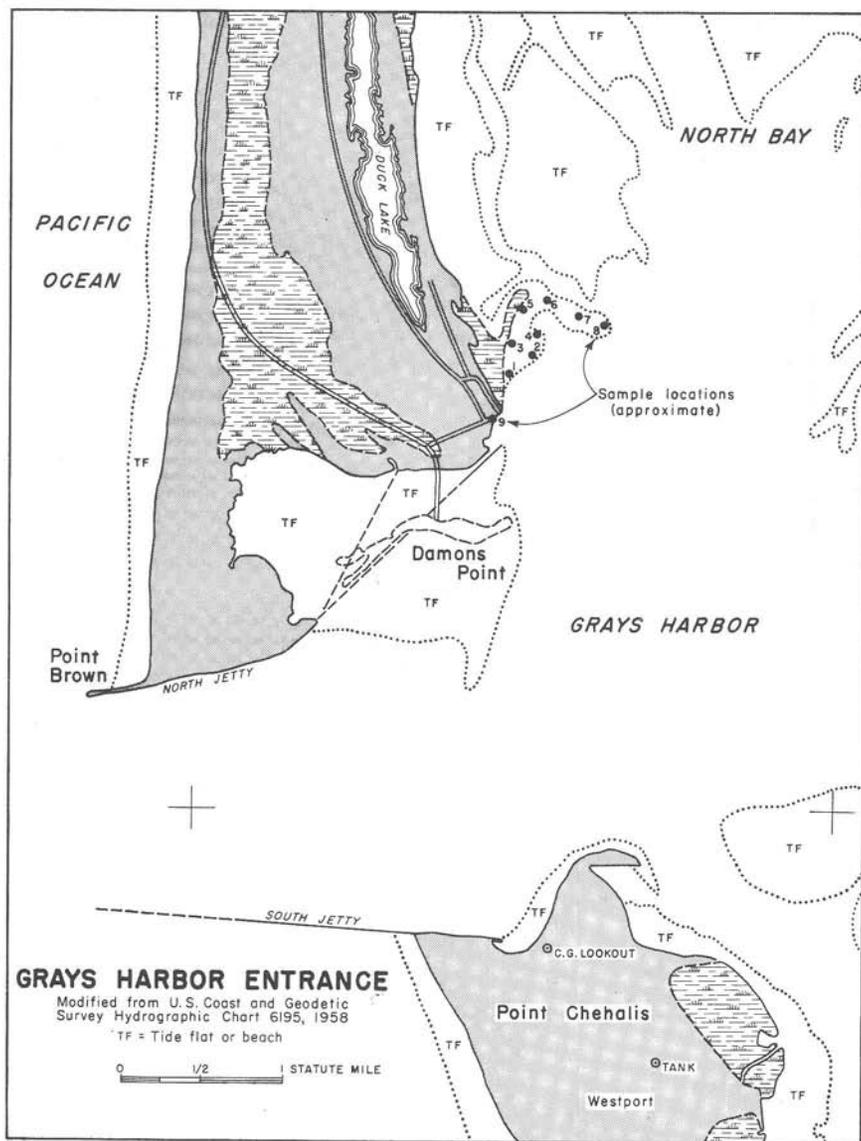


FIGURE 1.— Location map.

marine shales, siltstones, sandstones, and conglomerates. The volcanic rocks consist largely of basaltic flows, breccias, and pyroclastics. A few small intrusive bodies, generally gabbro porphyry and porphyritic basalt, also of Tertiary age, are known in the area.

An additional source of material is deposits left by continental glaciation. These were derived from a wide variety of igneous, metamorphic, and sedimentary rocks in the northern Cascade Mountains and adjacent areas in Washington and Canada. They were deposited over large areas in Thurston and Lewis Counties, where they were picked up by the Chehalis River system and carried to Grays Harbor.

PREVIOUS WORK

Day (Day and Richards, 1906) examined hundreds of samples of placer sands from throughout the western states. Several samples from the Grays Harbor area included two that can be located on a map. He reported 1.1 and 20.6 per cent olivine in these samples. In his text Day mentions that olivine and hypersthene were concentrated together by the methods he used. He apparently combined them and reported the total as olivine. This no doubt explains the reported presence of olivine here whereas this writer found none.

Day reported 2 cents and 5 cents in combined gold and platinum in his samples (based on \$80 per ounce for platinum and \$20 per ounce for gold). As neither exact ratios nor absolute quantities were reported, no correction for today's prices can be made.

Sixteen holes were drilled in June 1958 by the United States Bureau of Mines under the direction of Dean Holt. These holes were located along the south tip of the peninsula north of the Grays Harbor entrance and were as deep as 44 feet. The report of this work is now in preparation.

A University of Washington Master's thesis entitled "Recent Marine Sediments in Grays Harbor, Washington" was completed in 1963 by John Douglas Milliman. It discusses all aspects of the sediments and sedimentation in Grays Harbor but is largely devoted to size analyses of the sediments.

ACKNOWLEDGMENTS

The author gratefully acknowledges the suggestions and encouragement of Mr. Marshall T. Huntting, who originally proposed the project. Thanks are also due Mr. Vaughn E. Livingston, who helped collect the samples and critically

read the manuscript, and Dr. W. A. G. Bennett, who aided in the interpretation of the spectrographic analyses and in some of the mineral identifications. Zirconium-hafnium ratios reported on page 24 were provided by the United States Geological Survey.

SAMPLING

The area in which the nine samples were taken is in the tidal zone approximately 1,000 to 1,500 yards east of the southern tip of Duck Lake (fig. 1). Seven samples, averaging roughly 35 pounds (dry weight) each, were taken with a device used for digging razor clams. It consists of a sheet-metal pipe about 4 inches in diameter and 2 feet long, capped at one end. At the capped end a cross-handle is attached; near the handle is a hole about $1/3$ inch in diameter. When the device is pushed into the sand, displaced air escapes through the hole. When the handle end has been driven flush with the sand surface, one's thumb is placed over the air hole, creating a vacuum within the pipe as it is withdrawn. This prevents the column of sand within from sliding out. Three of these columns of sand were taken in line, 20 feet apart, for each of these seven samples. Sample No. 4 was taken with a shovel from a 6-inch layer of sand underlain by pebbles that prevented the use of the "clam gun." Sample No. 9 was scraped from the lower 4 feet of a 7-foot wave-cut vertical bank in an area of tree- and brush-covered stabilized sand dunes. A sampling interval of 200 to 300 yards was maintained wherever practical; however, this interval was modified in places by the low-tide beach outline and by local clay or shell beds. A 1- to 2-kilogram cut of each sample was saved for mineralogical studies, and the remainder was sent to a large iron-mining company for beneficiation tests and analytical work. Their data are reported on pages 24 to 27.

TREATMENT OF SAMPLES

Cuts of Samples 1, 3, and 5 were taken for sieve and heavy-liquid analysis. As No. 5 was the richest in heavy minerals, it was selected for more detailed mineralogical studies.

The samples were clean sand, so they did not require preliminary washing. They were screened for 12 minutes on a Ro-tap mechanical sieve shaker using 42-, 60-, 80-, 100-, 150-, and 200-mesh Tyler screens. The total of the material retained on 42-mesh and that passing the 200-mesh amounted to approximately 3 percent of Sample No. 5 and 4.5 percent of Sample No. 3. Sample No.

1, the lowest grade of the three, contained almost 10 percent material outside these size limits. This was almost entirely in the coarsest (plus 42 mesh) size range and consisted largely of shell fragments, root and bark fragments, and some coarse sand and fine pebbles. To remove the large proportion of quartz and feldspathic material prior to magnetic concentration, a bromoform separation was made of each sieve fraction.

Preliminary runs through the Frantz magnetic separator^{2/} indicated that hypersthene, garnet, and some of the black opaque minerals overlapped considerably in their magnetic susceptibilities. As these were the most abundant heavy minerals, it was desirable to try to isolate them for further study. To accomplish this, heavy-liquid separations were made, using liquids of 3.5 specific gravity (which floated the hypersthene from the garnet) and 4.3 specific gravity (which floated the garnet from the opaque blacks). The heavy liquid used was Clerici's solution (thallium malonate and thallium formate dissolved in water). Thus, before any magnetic separations were made, each of the five most abundant sieve fractions was broken down into four specific gravity ranges. These were of minerals whose specific gravities were less than 2.85, between 2.85 and 3.5, between 3.5 and 4.3, and those heavier than 4.3. At this point the heavier minerals could be seen to be concentrated in the finer sieve fractions (fig. 3). In fact, it was found that simply screening the raw sands of Sample No. 5 with an 80-mesh sieve and discarding the oversize approximately doubled the "grade." In other words, the total amount of sand is roughly halved (reduced even more in the lower grade samples), whereas only a minor amount of minerals heavier than 2.85 are lost. The following is a rough breakdown showing specific gravity distribution of the major minerals present. Each of these specific gravity ranges is discussed in detail, starting on page 11.

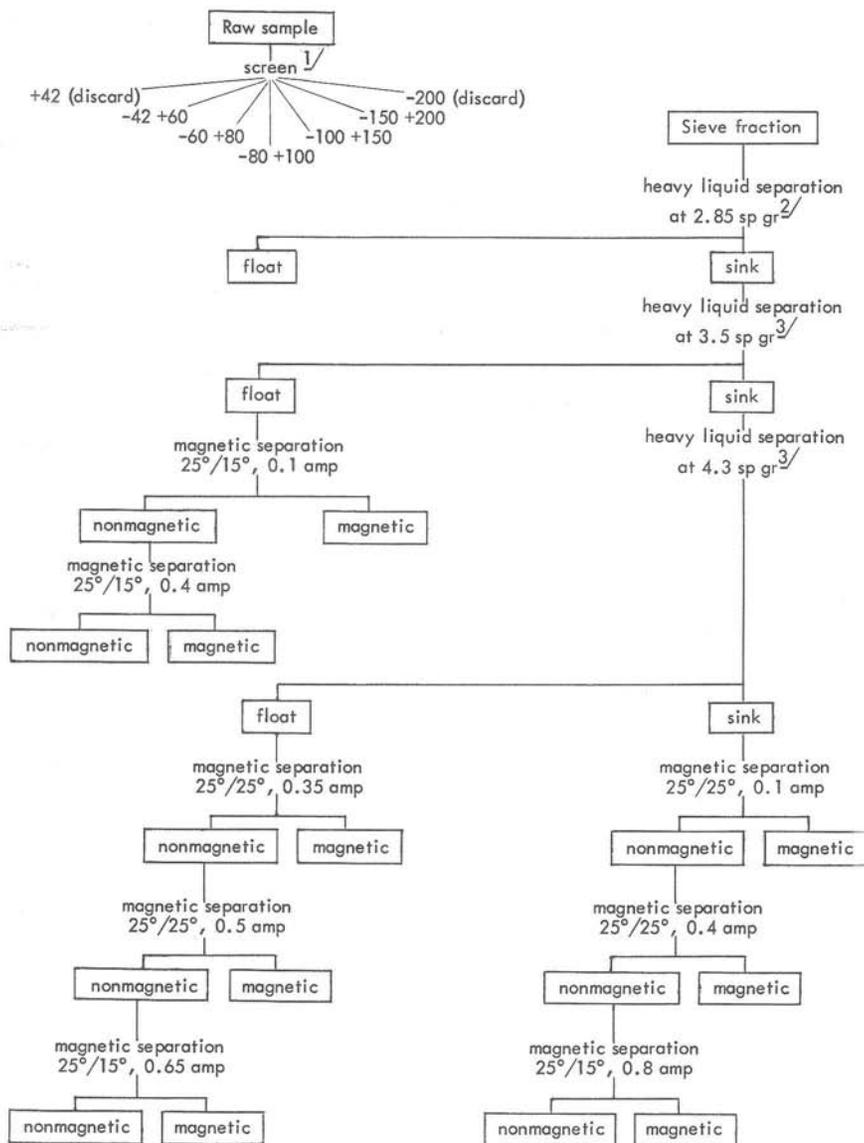
Less than 2.85—composed largely of feldspars, partially altered feldspars, and quartz.

2.85 to 3.5—composed largely of hypersthene but containing significant amounts of other ferromagnesian silicates.

3.5 to 4.3—composed largely of garnet but containing staurolite, kyanite, "unliberated magnetite-silicate" grains, and rutile.

Over 4.3—composed almost entirely of ilmenite, hematite, and magnetite (much of which is in the form of intergrowths), and some zircon.

^{2/} An extremely powerful laboratory electromagnet of variable intensity capable of separating materials not commonly considered magnetic.



1/ Tyler screen designated in mesh per inch.

2/ Bromoform.

3/ Clerici's solution.

4/ All magnetic separations made with Frantz Isodynamic Separator.

FIGURE 2. — Flowsheet.

TABLE 1.—Distribution of specific gravity ranges

Sieve size ranges	Specific gravity ranges	Percent of Sample No. 1	Percent of Sample No. 3	Percent of Sample No. 5
+42		9.33	0.44	2.15
-42 +60	-2.85	28.1	12.4	7.98
	2.85-3.5	1.3	1.37	2.53
	3.5-4.3	0.03	0.06	0.22
	+4.3	<u> </u>	<u>0.02</u>	<u>0.08</u>
	Total	29.43	13.85	10.81
-60 +80	-2.85	24.5	33.9	19.4
	2.85-3.5	1.83	5.69	14.2
	3.5-4.3	0.08	0.42	1.39
	+4.3	<u> </u>	<u>0.20</u>	<u>0.45</u>
	Total	26.41	40.21	35.44
-80 +100	-2.85	17.4	20.1	9.75
	2.85-3.5	1.3	4.10	13.7
	3.5-4.3	0.14	0.36	2.24
	+4.3	<u> </u>	<u>0.28</u>	<u>2.51</u>
	Total	18.84	24.84	28.20
-100 +150	-2.85	13.2	8.23	3.2
	2.85-3.5	1.33	4.95	6.62
	3.5-4.3	0.26	0.64	2.67
	+4.3	<u> </u>	<u>0.94</u>	<u>7.65</u>
	Total	14.79	14.76	20.14
-150 +200	-2.85	0.21	0.23	0.06
	2.85-3.5	0.36	0.47	0.23
	3.5-4.3	0.19	0.20	0.24
	+4.3	<u> </u>	<u>0.78</u>	<u>2.42</u>
	Total	0.76	1.68	2.95
-200		0.40	4.2	0.26
	Grand total	100.0	100.0	100.0

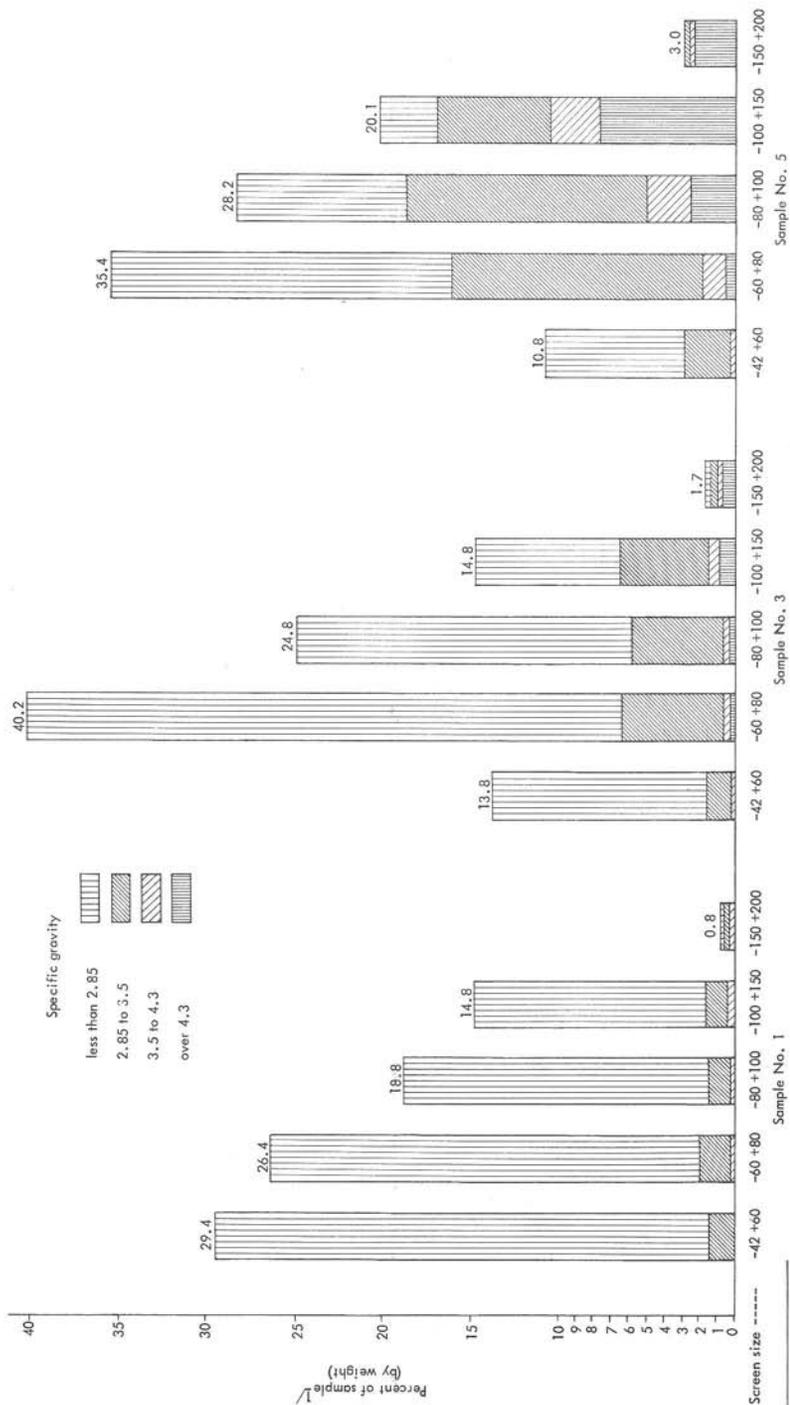


FIGURE 3. — Graph showing distribution of specific gravity ranges.

At this stage magnetic separations were begun in an attempt to isolate as nearly as possible the main heavy mineral constituents. As can be seen in the descriptions of the mineral concentrates starting on page 14, this was only partially successful. No doubt the separations would have been more successful if the two methods used, gravity and magnetic, were supplemented by electrostatic methods. The flow sheet (fig. 2) on page 8 shows the entire separation procedure used.

Mineral percentages are based on grain counts, or estimates in some cases, which yield volume percent. However, as the individual counts were on mineral concentrations within a relatively narrow specific gravity range, no corrections were made in converting to weight percent of the whole sample. Identification of transparent minerals was by petrographic microscope and refractive index oils.

RESULTS OF SEPARATIONS

Sample No. 5 was subjected to the entire procedure shown on the flow-sheet (fig 2), and the four most magnetic fractions were submitted for chemical analysis (table 2, on p. 20). Sample No. 3 was screened and split with heavy liquids, but no magnetic separations were made of fractions lighter than 3.5 specific gravity. Heavy-liquid separations only were made on the sieve fractions of Sample No. 1.

SPECIFIC GRAVITY LESS THAN 2.85

(84 percent of Sample No. 1, 75 percent of Sample No. 3,
40 percent of Sample No. 5)

This fraction was scanned briefly and found to contain about 25 percent quartz. Most of the rest of the material is opaque or translucent because of inclusions and (or) alteration. For this reason it is difficult to estimate the proportion of feldspar present; however, it is thought to be less than the quartz. A fairly close estimate of the feldspar content probably could be made by using staining techniques, but because of the lack of economic potential in this fraction, staining and grain counts were not done. Altered ferromagnesian silicates compose the bulk of the remainder of this specific gravity fraction.

SPECIFIC GRAVITY GREATER THAN 2.85, LESS THAN 3.5

(6.1 percent of Sample No. 1, 16.9 percent of Sample No. 3,
37.3 percent of Sample No. 5)

General

Hypersthene is so abundant in this specific gravity range that it could almost be called a concentrate. It makes up more than 50 percent of the material in this range and occurs as two varieties, both in the form of elongated crystals, octagonal in cross section. One variety, which is black and opaque, apparently owes its color to pigmentation by microscopic magnetite evenly dispersed throughout the crystals. These crystals are always highly magnetic, even when the inclusions are too fine to resolve under the microscope. Another characteristic of this variety is that when the crystals are intact they have a thin rind of earthy reddish material, which appears to be hematite. The second variety, which concentrates over a wide magnetic range, has a clear yellowish olive-brown color. This latter variety usually contains scattered magnetite inclusions ranging in size from those visible only under a microscope to those making up almost half the grain.

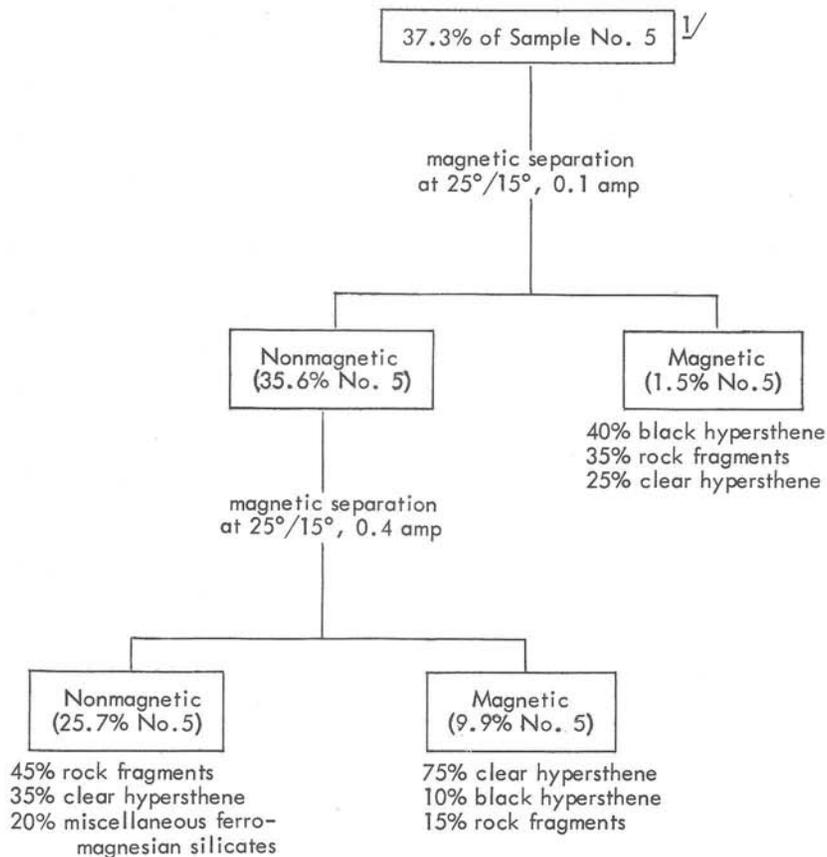
Although no actual grain counts were made on this specific gravity fraction, the estimates of mineral percentages of Sample No. 5 were made on each of the closely sized sieve fractions. These were then averaged to yield what is believed to be a fairly close approximation of the proportions of mineral constituents. The hypersthene makes up approximately 20 percent of Sample No. 5.

The 2.85 to 3.5 specific gravity range of Sample No. 5 was separated magnetically on the Frantz separator into three fractions, which are described below in order of decreasing magnetic susceptibility. Separations were made at slope settings of 25°/15°. ^{3/}

^{3/} On the Frantz separator both the magnet and the mineral chute that passes between the pole pieces adjust as a unit on two axes. Facing the instrument, with flow of material from right to left, a setting of 25°/15° corresponds to an angle of 25 degrees (from horizontal) sloping to the left and 15 degrees (from vertical) on the "side slope."

Specific Gravity 2.85 to 3.5

(6.1% of Sample No. 1, 16.9% of Sample No. 3, 37.3% of Sample No. 5)

^{1/} Only Sample No. 5 was separated magnetically.

Note.—Mineral percentages shown are based on estimates.

FIGURE 4.—Mineral content of magnetic fractions in the 2.85 to 3.5 specific gravity range.

Magnetic at 0.1 amp

(1.5 percent of Sample No. 5)

This fraction consists of approximately one-fourth clear hypersthene containing scattered magnetite inclusions and three-fourths rock fragments and black hematite-coated hypersthene in roughly equal amounts. The coated hypersthene proportion remains fairly constant from the coarse (minus 42 mesh) to the finer (plus 150 mesh) sizes. The clear hypersthene proportion increases as the grains become finer, whereas the proportion of rock fragments decreases in the finer sizes. The amount of other minerals present in this magnetic fraction is relatively insignificant.

Magnetic at 0.4 amp

(9.9 percent of Sample No. 5)

This magnetic fraction is more than three-fourths clear hypersthene containing fine irregularly scattered magnetite inclusions. Many of these grains appear to contain less than 5 percent magnetite. Hematite-coated hypersthene makes up about 10 percent of the magnetic fraction, and this proportion seems to remain fairly constant throughout the size range. The remainder is made up largely of rock fragments in the coarser sieve sizes, and miscellaneous mineral grains in the finer. This is no doubt merely a result of the liberation of the individual mineral grains as a rock fragment is broken into finer sizes.

Nonmagnetic at 0.4 amp

(25.7 percent of Sample No. 5)

No coated hypersthene is present in this fraction. Clear hypersthene percentages vary from about 10 percent in the coarsest size to 60 percent in the -150+200 mesh size. It constitutes about a third of the total magnetic fraction.

Miscellaneous materials (consisting largely of rock fragments) make up about 50 percent of this magnetic fraction, varying from 80 percent of the coarsest grains down to about 15 percent of the finest grains. Over 10 percent of the entire magnetic range is made up of assorted black ferromagnesian silicates. The remainder of the magnetic fraction (approximately 5 percent) consists of epidote.

SPECIFIC GRAVITY GREATER THAN 3.5, LESS THAN 4.3
(0.7 percent of Sample No. 1, 1.7 percent of Sample No. 3,
6.8 percent of Sample No. 5)

General

A heavy liquid adjusted to 3.5 specific gravity (Clerici's solution) was used to separate the abundant hypersthene from garnet and other heavier silicates such as kyanite and staurolite. The magnetic susceptibility of the hypersthene varied over such a wide range that it was impossible to make this separation magnetically. The magnetic fractions of this specific gravity group are described below in order of decreasing magnetic susceptibility. As Sample No. 1 contained too little of this material to handle conveniently, it was not separated into magnetic fractions.

Counts of between 350 and 400 grains of Sample No. 5 were made in determining the mineral percentages reported in this gravity fraction.

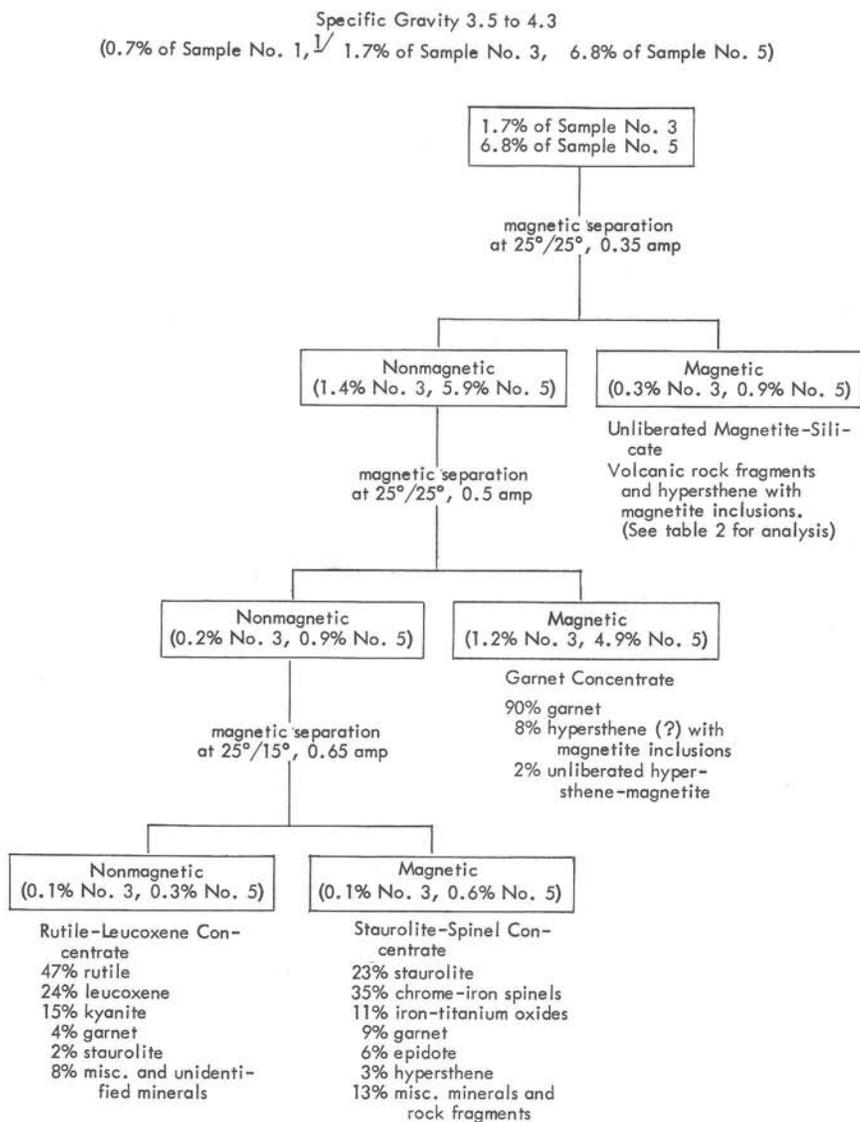
Unliberated Magnetite-Silicate (Magnetic at 25°/25°, 0.35 amp)
(0.3 percent of Sample No. 3, 0.9 percent of Sample No. 5)

Examination of these fractions with a binocular microscope reveals the coarser sieve sizes to be made up largely of volcanic rock fragments containing one or more large grains of magnetite.

The finer grain sizes appear to be mainly opaque black silicate minerals, many of which appear to be hypersthene. Their opacity, high magnetic susceptibility, and high specific gravity are apparently caused by what appear to be dense black "clouds" of microscopic magnetite grains. Less dense streaks of this pigmentation can be seen in partly transparent hypersthene grains from the 2.85 to 3.5 specific gravity range.

Garnet Concentrate (Magnetic at 25°/25°, 0.5 amp)
(1.2 percent of Sample No. 3, 4.9 percent of Sample No. 5)

This concentrate consists of approximately 90 percent garnet, the remainder being made up of 8 percent translucent and opaque unidentified blacks (probably hypersthene with magnetite inclusions; see preceding paragraph), and 2 percent "unliberated" transparent hypersthene-magnetite (those containing magnetite inclusions visible with the unaided eye).



^{1/} Because of the small amount of this gravity concentrate, no magnetic separations were made.

Note. — Mineral percentages are based on counts of 350 to 400 grains of Sample No. 5.

FIGURE 5. — Mineral content of magnetic fractions in the 3.5 to 4.3 specific gravity range.

The garnet is mostly a very pale pink variety with a refractive index of slightly over 1.80. This plus strong manganese tests indicate that it is near the spessartite end of the almandite-spessartite series and probably has a specific gravity of about 4.2 (Winchell and Winchell, 1951, p. 487). Some yellowish andradite garnets (index approximately 1.89) can also be seen. The garnet grains are mostly rather angular. They are confined largely to the -60 +150 mesh size range, with only minor amounts beyond these limits. In the samples examined, practically none of the garnet was coarser than 42 mesh or finer than 200 mesh.

Staurolite-Spinel Concentrate (Magnetic at 25°/15°, 0.65 amp)

(0.1 percent of Sample No. 3, 0.6 percent of Sample No. 5)

Staurolite is the most abundant positively identified mineral species in this magnetic fraction, constituting 23 percent of the fraction. Opaque blacks tentatively identified as being chrome-iron varieties of the spinel group make up 35 percent of this concentrate. These have a submetallic luster, and many of the grains are octahedra or fragments of octahedra. Another group of black opaques with what appear to be thin irregular reddish and, on some, reddish-white coatings, form 11 percent of this concentrate. Spectrographic analysis of some of these grains, selected with care under the binocular microscope in an effort to eliminate contamination, show them to be high in titanium, iron, and silica; considerable magnesium is also present. The high silica content seems to rule against its being entirely rutile, whereas the relatively minor amount of calcium present rules out titanite. The probable explanation is that, in spite of precautions, some composite grains and (or) a few ferromagnesian silicate grains were included in the sample. These reddish-coated opaques are tentatively classified as leucoxene-hematite-coated rutile-hematite intergrowths. Garnet (mainly spessartite) makes up 9 percent, and a high-iron variety of epidote forms another 6 percent. About 3 percent is hypersthene, and approximately 13 percent is composed of miscellaneous and unidentified minerals and rock fragments.

Rutile-Leucoxene Concentrate (Nonmagnetic at 25°/15°, 0.65 amp)

(0.1 percent of Sample No. 3, 0.3 percent of Sample No. 5)

This fraction collects on the "nonmagnetic" side at 0.65 amp. It was found to contain approximately 48 percent rutile. That this rutile is not pure TiO_2 was

demonstrated by spectrographing what appeared to be two different varieties. Both samples were handpicked under a binocular microscope, and both the adamantine black and the dark-brown resinous varieties had essentially the same spectrograms. These showed, in addition to the expected large amount of titanium, significant quantities of iron, silica, aluminum, calcium, and chromium. Traces of zirconium and vanadium were also observed.

Leucoxene was identified on the basis of its physical and chemical properties, appearing as rounded gray opaque grains and having a chemical composition nearly identical with the rutile previously mentioned. It makes up 24 percent of this magnetic fraction.

Kyanite makes up 15 percent of this fraction and is readily identified as clear tabular rectangles, with most of the grains displaying a perfectly centered acute bisectrix interference figure when examined under the polarizing microscope.

The remainder of this magnetic fraction consists of 4 percent garnet, 2 percent staurolite, and 8 percent miscellaneous and unidentified minerals. A considerable amount of this 8 percent was epidote, which probably occurred here because of incomplete heavy-liquid separations of some sieve fractions. A few grains of clear and transparent-blue corundum were also noted.

SPECIFIC GRAVITY: GREATER THAN 4.3

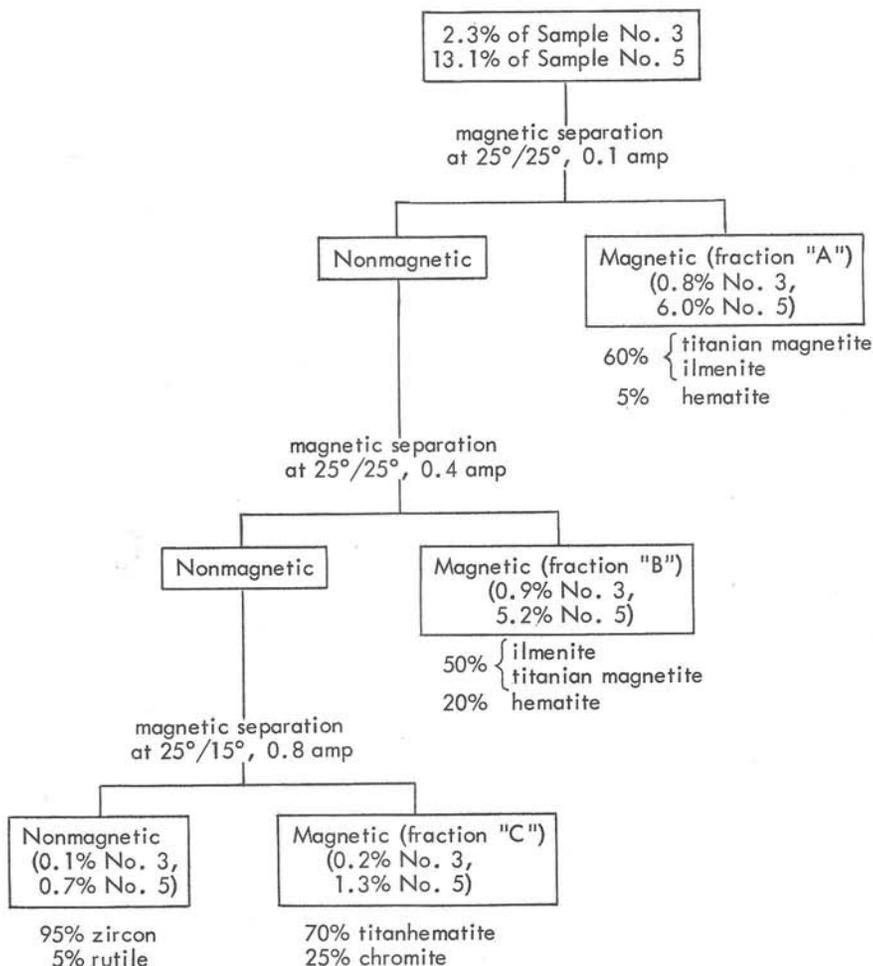
(Approximately 0.5 percent of Sample No. 1, 2.3 percent of Sample No. 3, and 13.1 percent of Sample No. 5)

General

Bakelite mounts of the mineral grains in the -80+100 mesh fraction for each sample were prepared and polished, for examination under a metallographic microscope with cap analyzer. Color, estimated reflectivity, and whether the grain was isotropic or anisotropic were the characteristics used for identification. As variations in composition (solid solution effects) may alter the first two, and grain orientation affects the last, some identifications were based on indirect evidence such as magnetic susceptibility. For this reason, relative proportions of the opaques are considered to be approximations, and fewer grains were counted than in the transparent mineral fractions.

Examination of the analyses (table 2, on p. 20) shows a lack of sharp contrast in composition between fractions of rather widely varying magnetic susceptibilities. The fact that the iron content remained high (36.9 percent) even on the

Specific Gravity Greater Than 4.3

(0.5% of Sample No. 1, ^{1/} 2.3% of Sample No. 3, 13.1% of Sample No. 5)

^{1/} Because of the small amount of this gravity concentrate, no magnetic separations were made.

Note. — Mineral percentages shown are based on estimates.

FIGURE 6. — Mineral content of magnetic fractions in the plus 4.3 specific gravity range.

TABLE 2. — Chemical analyses of black opaque mineral concentrates in Sample No. 5. ^{1/} Head sample contained 12.78 percent iron (see table 6).

Magnetic susceptibility	Sieve size range	Percent by weight	Percent sp gr range	Percent of entire sample	Analysis						Distribution (percent)			Radio-activity
					Calculated as oxide			Fe			Fe	Ti	Cr	
					TiO ₂	Cr ₂ O ₃	Cr	Ti	Cr					
PLUS 4.3 SP GR														
MAGNETIC FRACTION "A" (magnetic at 0.1 amp)	-60 +80 -80 +100 -100 +150 ^{3/} -150 +200	3.6 19.7 59.4 17.3			44.85 20.86 43.70 20.86 44.51 21.44 46.02 20.96	2/ 2/ 2/ 2/ 2/ 2/ 2/ 2/	34.80 34.80 35.76 34.96	3.7 19.3 59.2 17.8	3.6 19.4 59.9 17.1	2/ 2/ 2/ 2/ 2/ 2/ 2/ 2/				
	Total ----- Weighted average -----	100.0 45.9	6.0	44.6	21.2				100.0 100.0					
MAGNETIC FRACTION "B" (magnetic at 0.4 amp)	-60 +80 -80 +100 -100 +150 -150 +200	3.2 18.4 59.2 19.2			42.54 23.00 40.69 24.14 41.39 24.66 40.69 25.16	0.36 0.41 0.25 0.27	38.36 40.27 41.13 41.97	3.3 18.2 59.5 19.0	3.0 18.1 59.2 19.6	2/ 2/ 2/ 2/ 2/ 2/ 2/ 2/				
	Total ----- Weighted average -----	100.0 39.2	5.2	41.2	24.6	0.29			100.0 100.0					
MAGNETIC FRACTION "C" (magnetic at 0.8 amp)	-60 +80 -80 +100 -100 +150 -150 +200	6.5 28.5 55.2 9.8			39.19 19.89 37.34 19.99 36.31 20.77 36.65 18.72	7.65 7.44 7.15 7.44	33.18 33.34 34.65 31.23	6.9 28.9 54.5 9.7	6.4 28.1 56.5 9.0	0 0 0 Trace				
	Total ----- Weighted average -----	100.0 9.8	1.3	36.9	20.3	7.3			100.0 100.0					
3.5 to 4.3 SP GR														
MAGNETIC AT 0.35 AMP	-60 +200				30.41	16.67								2/
	Total -----	100.0	0.9											

^{1/} Analyses by Peter Kangers, Washington State University, Institute of Technology, Division of Industrial Research.
^{2/} Not analyzed.
^{3/} The most magnetic part (19 percent) of this fraction was separated by hand magnet and yielded 51.4 percent Fe and 15.0 percent Ti (25.0 percent TiO₂). Analysis by Willis Orr, Metallurgical Laboratories, Seattle.

nonmagnetic fraction at 0.4 amp, was rather surprising. This was readily explained, however, when microscopic examination showed the presence of abundant hematite. Intergrowths of ilmenite, hematite, and magnetite in all combinations and proportions (usually only two in a given grain, however) also contributed to the lack of contrast in composition. Because of the similarity between the fractions magnetic at 0.1 amp and at 0.4 amp, they are simply designated as "A" and "B," respectively, and described together below.

As neither precious metals nor radioactive minerals were identified, no analyses were made for these.

Magnetic Fractions "A" and "B"

("A" magnetic at 25°/25°, 0.1 amp)

("B" magnetic at 25°/25°, 0.4 amp)

(1.7 percent of Sample No. 3, 11.2 percent of Sample No.5)

Probably the most striking feature of these magnetic fractions is the almost complete absence of pure magnetite. Only a relatively few grains were deeply etched, even after 20 seconds' immersion in concentrated hydrochloric acid, and these were all in fraction "A." An isotropic mineral present in both fractions, not etched by the acid, was identified as titanium-rich magnetite. As magnetite can carry up to 7.5 percent TiO_2 in solid solution (Palache, Berman, Frondel, 1944, p. 702), it seems very likely that the mineral's resistance to corrosion would be sufficiently affected to account for this anomalous lack of an etch reaction. This titanium-rich magnetite and ilmenite together made up between 50 and 60 percent of both "A" and "B." No intergrowths could be seen in the ilmenite at 250-power magnification; however, it is likely that magnetite is present in intergrowths beyond the resolving power of the microscope, which would account for the grains' highly magnetic nature.

Hematite makes up a small percentage of "A" and comprises roughly 20 percent of "B." The hematite probably formed through the alteration of magnetite. Some unaltered magnetite remains in the grains, causing them to concentrate in this magnetic range. Most of the remaining grains of both "A" and "B" are made up of intergrowths of magnetite, hematite, and ilmenite. Some grains, however, contain inclusions of what appears to be rutile.

A cut of the -100+150 mesh size "A" fraction (25°/25°, 0.1 amp) of Sample No. 5 was split with a hand magnet (0.1 amp is the weakest setting on the Frantz

separator) in an attempt to get a higher grade iron concentrate. That portion of "A" was collected which could be picked up by a small Alnico hand magnet held half an inch vertically above the sample. In this way a concentrate was obtained that represented the most magnetic 19 percent of fraction "A." (A cut at this magnetic intensity of all sieve sizes would make up approximately 1.1 percent of the entire Sample No. 5.) This cut was assayed and found to contain 51.4 percent Fe, an increase of 6.8 percent over the weighted average found in fraction "A" (table 2, on page 20). This increase in the iron content was accompanied by a similar decrease (6.2 percent) in the titanium content from the average of 21.2 percent found in fraction "A" to 15.0 percent found in this highly magnetic split. The trend could probably be continued, taking successively smaller proportions of the sample by using progressively weaker magnetic fields. There is little doubt that if this were continued far enough one could obtain a concentrate of pure titanium-free magnetite. It is extremely doubtful that this would be economical, however, as the pure magnetite content appears to be far too low to merit the expense of separate treatment.

The possibility that a richer iron or titanium concentrate could be obtained at extremes in the grain size range was considered because of the probably diverse parent-rock types. For this reason, different grain sizes for a given magnetic susceptibility were assayed separately (table 2, on page 20). No strong trends were apparent from these assay data. However, the "B" fraction (magnetic at 25°/25°, 0.4 amp) shows a gradual increase in titanium as the grain size decreases. In this same magnetic fraction there seems to be a slight decrease in iron content as the grain size diminishes. This same trend appears to be repeated in the less magnetic "C" fraction. These trends are too gradual to be of any direct commercial significance, however, and it would be of little economic importance even if they changed abruptly near the extremes in grain size. This is apparent when one notes that only 13 percent of this entire sample (No. 5) falls outside of the size range represented in the assays and that the proportion of heavy blacks that falls outside these same limits is insignificant. Possibly some strong trends would have been apparent in the minus 200 mesh grain sizes, but there was so little material that no detailed work was possible.

A comparison of all sieve fractions in all specific gravity ranges magnetic at 0.4 amp on the Frantz separator is interesting. Disregarding specific gravity differences, approximately 23.5 percent of Sample No. 5 is magnetic at this field intensity. Of the grains in this magnetic range, less than half (11.2 percent of Sample No. 5) are in the form of iron-titanium oxides. The remainder are hyper-

sthene with magnetite inclusions (float at 3.5 sp gr) and some "unliberated magnetite-silicates" (float at 4.3 sp gr). Attempts to obtain a cleaner concentrate, at the price of heavy tailings loss, by reducing the magnetic field strength (to 0.1 amp on the separator) were also frustrated. This setting, at which about half of the iron-titanium oxides were rejected as nonmagnetic, yields a concentrate still containing approximately 20 percent hypersthene.

Magnetic Fraction "C" (Hematite Concentrate)

(Magnetic at 25°/15°, 0.8 amp)

(0.2 percent of Sample No. 3, 1.3 percent of Sample No. 5)

This fraction, although in the same gravity range (sp gr greater than 4.3) as "A" and "B" and also consisting of opaque blacks, is considerably less magnetic than "A" and somewhat less than "B." Another important difference is the presence of chromium (7.3 percent). Spectrographic analysis also showed slightly more aluminum in this fraction than in "A" or "B." The aluminum could be accounted for as a substitute for the chromium in the chromite-hercynite solid solution series (Deer, Howie, and Zussman, 1962, p. 64). Polished sections of mineral grains in fraction "C" show less than in "A" and "B." This fraction appears to be made up almost entirely of titanhematite (hematite containing up to 10 percent TiO_2 in solid solution) (Uytenbogaardt, 1951, p. 197) and chromite (about 25 percent). The identification of titanhematite is indirect and is largely based on the abundance of a mineral appearing to be hematite, the absence of other titanium-bearing minerals, and the presence of 20.3 percent titanium in the fraction. Many of these polished grains are minutely pitted, and some contain what appear to be rutile inclusions. Possibly the pits are the result of finer inclusions being "plucked out" during polishing. If so, this would easily account for the TiO_2 content of this fraction. A few grains of iron-titanium-bearing intergrowths and rutile are the only "impurities" in this fraction.

Zircon Concentrate (Nonmagnetic at 25°/15°, 0.8 amp)

(0.1 percent of Sample No. 3, 0.7 percent of Sample No. 5)

This fraction, which is almost pure zircon, concentrates on the nonmagnetic side on the Frantz separator at a setting of 25°/15°, 0.8 amp. Most of the

grains are angular; however, grains ranging from elongated doubly terminated crystals to almost perfect spheres are common. Over two-thirds (estimated) of the grains are transparent and colorless. The rest are largely a very pale orange or a pale purple color. The impurities present in minor amount (estimated as less than 5 percent) in this zircon concentrate seem to be largely rutile. X-ray fluorescence analyses were run by Richard R. Larson, U.S. Geological Survey, on two different size fractions (-80+100 mesh and -150+200 mesh) of the zircon concentrate of Sample No. 5. These yielded hafnium/zirconium ratios of 0.023/1 and 0.025/1 respectively.^{1/} These figures actually represent the average of many grains, probably with wide variations from grain to grain, as the samples submitted contain zircon from diverse rock types from over a broad drainage area. Some of this drainage is from areas covered by outwash from Puget Sound continental glaciation.

Forty analyses of zircon from all over the world show hafnium/zirconium ratios ranging from 0.002/1 to 0.100/1, with a mean of 0.027/1 (Mertie, 1958, p. 14). Thus the analyses of the composites of grains from Grays Harbor are not far from this mean.

BENEFICIATION TESTS

Approximately 35 pounds of sand from each of the nine holes was sent in April 1958 to a major company for beneficiation tests. All the following data are from the company's report on its tests of these samples.

A portion of each individual sample as received by the company was screened on 10 mesh for the removal of sea shells, rock fragments, and roots. The minus 10 mesh material was split into representative portions for assay and test work. Assay results are shown in table 3.

^{1/} In nature, a small amount of hafnium is always found in zirconium-bearing minerals, and ordinary chemical analyses for zirconium state in reality the sum of zirconium and hafnium (Mertie, 1958, p. 2). This is because of the very similar chemical properties of the two elements. As they have different physical properties, however, certain specialized uses may require their separation. Thus, the hafnium content may be of particular interest.

TABLE 3.—Crude sand analyses

Sample number	Plus 10 mesh Percent by weight ^{1/}	Minus 10 mesh	
		Percent by weight	Percent Fe
1	Trace	100.0	2.61
2	Trace	100.0	3.21
3	4.3	95.7	4.45
4	1.4	98.6	4.60
5	0.7	99.3	12.78
6	5.5	94.5	3.76
7	Trace	100.0	3.97
8	Trace	100.0	4.92
9	0.6	99.4	6.43

^{1/} Trace indicates less than 0.1 percent by weight.

Davis tube tests were run on the minus 10 mesh material to determine the magnetite content. These results show that the magnetite content of these sands is low and that a poor degree of liberation exists.

TABLE 4.—Davis tube concentrate analyses

Sample number	Percent by weight of crude sand	Percent iron (Fe)	Percent of recovered iron	Ratio of concentration
1	0.5	16.59	2.7	200.0
2	0.8	26.12	6.2	125.0
3	1.5	36.21	12.1	66.7
4	1.4	30.25	8.9	71.4
5	8.6	45.46	30.6	11.6
6	1.0	33.76	9.8	100.0
7	1.9	35.91	17.1	52.6
8	1.8	37.32	13.6	55.6
9	4.0	26.88	16.8	25.0

A portion of the minus 10 mesh head of each sample was concentrated on a Wilfley table to obtain a concentration of the higher specific gravity minerals for microscopic examination. All these samples contain a high proportion of hypersthene that tends to concentrate with the "heavier" minerals, and a low-grade concentrate resulted.

Microscopic examination of the table concentrates indicates that ilmenite is the most abundant mineral of possible commercial value in the sands. Magnetite and hematite are present in small amounts, and zircon and rutile are minor minerals. Hypersthene, quartz, and feldspar are the major minerals in the concentrates.

A tabulation of the titania (TiO_2) content of these sands based on the table test results is presented below. The titania occurs chiefly as ilmenite.

TABLE 5. — Wilfley table concentrate analyses

Sample number	Percent by weight of crude sand	Percent TiO_2	Pounds TiO_2 per long ton of crude sand
1	3.6	4.72	3.8
2	8.4	4.91	9.2
3	11.4	10.49	26.8
4	9.9	6.97	15.5
5	59.0	10.75	142.0
6	9.7	7.07	15.4
7	12.0	7.43	19.9
8	15.1	8.38	28.3
9	26.5	7.33	43.5

TABLE 6. — Analyses of Grays Harbor sands and concentrates

Sample number	Screen size (percent of crude sand)		Analytical results for -10 mesh					Wilfley table test	
	+½ in	-½ in +10 mesh	Davis tube test			Fe distribution (percent)	Fraction	Percent of crude sand	TiO ₂ (percent)
			Fraction	Percent of crude sand	Fe (percent)				
1	Tr	Tr	concentrate tailing heads	0.5 99.5 100.0	16.59 2.55 2.61	2.7 97.3 100.0	concentrate tailing heads	3.6 96.4 100.0	4.72
2	Tr	Tr	concentrate tailing heads	0.8 99.2 100.0	26.12 3.03 3.21	6.2 93.8 100.0	concentrate tailing heads	8.4 91.6 100.0	4.91
3	4.0	0.3	concentrate tailing heads	1.5 94.2 95.7	36.21 4.15 4.45	12.1 87.9 100.0	concentrate tailing heads	11.4 84.3 95.7	10.49
4	Tr	1.4	concentrate tailing heads	1.4 97.2 98.6	30.25 4.31 4.60	8.9 91.1 100.0	concentrate tailing heads	9.9 88.7 98.6	6.97
5	0.7	Tr	concentrate tailing heads	8.6 90.7 99.3	45.46 9.78 12.78	30.6 69.4 100.0	concentrate tailing heads	59.0 40.3 99.3	10.75
6	0.4	5.1	concentrate tailing heads	1.0 93.5 94.5	33.76 3.43 3.76	9.8 90.2 100.0	concentrate tailing heads	9.7 84.8 94.5	7.07
7	Tr	Tr	concentrate tailing heads	1.9 98.1 100.0	35.91 3.35 3.97	17.1 82.9 100.0	concentrate tailing heads	12.0 88.0 100.0	7.43
8	Tr	Tr	concentrate tailing heads	1.8 98.2 100.0	37.32 4.33 4.92	13.6 86.4 100.0	concentrate tailing heads	15.1 84.9 100.0	8.38
9	0.0	0.6	concentrate tailing heads	4.0 95.4 99.4	26.88 5.61 6.43	16.8 83.2 100.0	concentrate tailing heads	26.5 72.9 99.4	7.33

SUMMARY

Iron and titanium oxides (largely intergrown) were the currently valuable minerals found in large enough quantities to be of possible commercial interest. The abundant heavy magnetic silicates will no doubt be a nuisance in any attempts to concentrate the oxides.

The relatively small amounts of fine-grained zircon and rutile might be economically recoverable on a byproduct basis.

No precious metals were found, although a previous study indicates both platinum and gold are present in very minor amounts.

No radioactive minerals were identified, but a trace of radioactivity was detected in magnetic fraction "C" (see table 2, on page 20).

REFERENCES CITED

- Day, D. T., and Richards, R. H., 1906, Useful minerals in the black sands of the Pacific slope: U.S. Geol. Survey Mineral Resources U.S. 1905, p. 1175-1258.
- Deer, W. A., Howie, R. A., and Zussman, J., 1962, Rock-forming minerals, v. 5, Non-silicates: New York, John Wiley & Sons, 371 p.
- Mertie, J. B., Jr., 1958, Zirconium and hafnium in the southeastern Atlantic States: U.S. Geol. Survey Bull. 1082-A, 28 p.
- Milliman, J. D., 1963, Recent marine sediments in Grays Harbor, Washington: Univ. of Washington M.S. thesis, 172 p.
- Palache, Charles; Berman, Harry; and Frondel, Clifford, 1944, The System of Mineralogy, 7th ed., v. 1, Elements, sulfides, sulfosalts, oxides: New York, John Wiley & Sons, 834 p.
- Pardee, J. T., 1929, Platinum and black sand in Washington: U.S. Geol. Survey Bull. 805, p. 1-15.
- University of Washington Department of Oceanography, 1955, Grays Harbor, Washington; a literature survey: Seattle, Univ. of Washington Dept. of Oceanography, 142 p.
- Uytenbogaardt, W., 1951, Tables for microscopic identification of ore minerals: Princeton, N. J., Princeton University Press, 242 p.
- Winchell, A. N., and Winchell, Horace, 1951, Elements of optical mineralogy, pt. 2, Descriptions of minerals: New York, John Wiley & Sons, 551 p.

