

AN INVESTIGATION OF THE GEOLOGICAL OCCURRENCE AND USE OF TITANIUM  
WITH SPECIAL REFERENCE TO  
THE SAN GABRIEL TITANIUM DEPOSITS, CALIFORNIA

By

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Fig. 1. - (Specimen Kath. 1). Section showing a fine grained "actinolite" type ore from the San Gabriel Titanium deposits. About 16 per cent of the slide is magnetite and ilmenite (black).

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INTRODUCTION -

It has been customary to class titanium with the rare elements, but in reality it is one of the most abundant of metals. Geochemists have estimated that it constitutes 0.44 per cent of the solid crust of the earth and ranks ninth in relative abundance of the ninety odd elements found there. It is more abundant than the common elements carbon, phosphorus, sulphur, and manganese, and exceeds the total of the common metals, lead, zinc, and copper. Titanium is also one of the most widely distributed of the elements.

Why then, has it not come into more common use during the one hundred and forty years since its discovery? There are two principal reasons: (1) Its great chemical tenacity which made it very hard to treat. (2) The fact that its minerals have shown no characteristics that make their usefulness readily apparent. In a narrow sense, it is true that titanium is seldom met with in nature in easily recognizable forms or in concentrations that readily attract attention; yet there are ample supplies available in commercial deposits.

For these reasons titanium compounds as articles of commerce were almost unknown until recent years. With the intensified interest now manifest in the utilization of the so-called rare metals, titanium is rapidly increasing in importance. Its rapid growth is well illustrated by the titanium pigment industry which has increased its consumption of ilmenite ( $\text{FeO-TiO}_2$ ) from 2,000 to 3,000 tons to over 100,000 tons a year in less than a decade. As technical improvements continue to remove its economic handicaps it is felt that titanium, because of its wide-spread distribution and abundance, will occupy an important place in the mineral industry.

The purpose of this thesis is: (1) to give a general outline of the titanium industry, (2) to present the results of a detailed study made of the ores of a titanium deposit in the San Gabriel Mountains near Los Angeles, California.

Part I treats titanium in a general way and outlines in brief the history of the industry, the properties of the element and its compounds, their geologic relations along with the resources and production of titanium compounds and their industrial uses. Of necessity, most of the information is obtained from the literature. Because, in general, the possibilities of the titanium industry are so little known, it is felt that such a compilation would be of value and interest.

Part II deals with the laboratory study of a magnetite-ilmenite ore of the San Gabriel Mountains. In it the results obtained from a detailed study of hand specimens, polished sections, and thin sections supplemented with some field work are given. The laboratory work was carried out at the California Institute of Technology during the year 1937-1938 in connection with tests made by the I. E. Dupont de Nemours Company on the magnetite-ilmenite deposits of the San Gabriel Mountains. (See Plate I for key map showing location of deposits.)

The author wishes to acknowledge the kindness of Dr. Joseph L. Gillson and Dr. G. H. Anderson of that company in permitting the presentation of part of the laboratory results from those tests. He wishes also to thank C. A. Dawson, the testing laboratory superintendent, and J. W. George, the field geologist, for their helpful interest. Co-workers on the problem were W. E. Snow and Richard H. Jahns, both of the California Institute of Technology. To these men the writer is indebted for assistance and kind cooperation. The work was done under the direction and guidance of Dr. H. J. Fraser, of the faculty of the California Institute of Technology.

## History

The element, titanium<sup>1</sup> \* was discovered about 1790, by the Rev. William Gregor (or McGregor) while investigating a peculiar mineral found in the form of black sand at Menachan in Cornwall, England. The black sand he named Menachanite after the locality in which it was found, and the new element he called Menachite.

In 1795 the German chemist Claproth<sup>2</sup>, while investigating the composition of rutile discovered a new metal, to which, because of the strength of the chemical combination in which it was held he gave the name, Titanium -- in allusion to the Titans, the symbol of strength in ancient Greek mythology. In subsequent investigation of ilmenite, Claproth recognized that titanium was identical with the menachite of Gregor. Titanium however, is the name that has been universally adopted. Lampadius, in 1797 and later, Berzelius and a number of other investigators attempted to isolate the new element. Due to its high fusion point and strong affinities for nitrogen, carbon, and oxygen, these early attempts to reduce titanium from its compounds were unsuccessful. The usual result was in the production of some of the nitrides or carbides which, on account of their metallic luster, were commonly mistaken for the metal itself. A copper red compound that we now know to be a cyanonitride of titanium was, until its true composition was demonstrated by Wohley in 1849, commonly believed to be metallic titanium. Probably Hunter<sup>3</sup> in 1910 succeeded in obtaining the first pure metallic titanium. Up to that time several attempts had been made to obtain the pure element; the nearest approach being that of a Frenchman, Henri Moissan, who obtained a titanium product that had only about 2 per cent carbon and a little oxygen as impurities.

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\*To avoid a needless repetition of footnotes, references in Part I are made by means of figures, corresponding with those of the numbered list given in the bibliography, at the end of Part I.



Hunter attempted a number of methods including those of Moissan, but was unsuccessful until he adopted one used earlier by Nilson and Peterson, which consisted essentially in reducing titanium tetrachloride ( $TiCl_4$ ) by means of sodium in an air-tight steel cylinder. The best results that Nilson and Peterson were able to obtain was a product containing about 79 per cent titanium; the chief impurity being oxygen, present presumably as titanium monoxide ( $TiO_2$ ). By exercising rigorous care to insure the exclusion of air from the apparatus used, Hunter succeeded in obtaining metallic titanium practically 100 per cent pure.

The Nilson-Peterson method as carried out by Hunter, is still the standard laboratory method for the production of pure metallic titanium, but is much too costly for its production for ordinary industrial purposes. A cheap commercial process for its manufacture in a substantially pure state has not yet been accomplished and little of the pure metal is used in industry today. Unimportant amounts of titanium of 96-98 per cent purity are used in the making of a high-speed steel in which titanium replaces vanadium.

Though the possibility of utilizing various compounds of titanium was suggested soon after the discovery of the element, it is only within comparatively recent years that any noteworthy progress has been made in this direction. Some examples of early developments follow. In 1846, the ferrocyanide of titanium was used as a green paint as an attempted substitute for the poisonous arsenical copper green then commonly used. In 1861, a patent was granted in London covering the use of certain compounds of titanium as pigments. About this same time Musset<sup>1</sup> took out several patents on the utilization of the ores of iron and titanium and for obtaining alloys of the two metals. In all, Musset took out some thirteen English patents, including one, the thirteenth and last, which covered the addition of "titanic pig-metal," to ordinary pig iron in a puddling furnace with a view to improving the quality of the iron or steel produced. In spite of the most vigorous efforts he failed to convince the ironmasters and metallurgists of his day of the surpassing excellence of his titaniferous steel, and the matter was dropped.

The credit for the establishment of the ferrotitanic alloy industry is due largely to August J. Rossi,<sup>4</sup> a French metallurgist, resident of the United States. His work in the 1890's led to the production of ferrotitanium and demonstrated its value for the purification of steel. After several unsuccessful attempts he succeeded, by means of the high temperatures obtainable in an electric furnace, in evolving an economical process for the manufacture of the high titanium alloys, ferrotitanium and ferrocarbon titanium. Although Rossi appears to have produced ferrotitanium by a practical industrial process prior to 1895, the possibilities of the new alloy were slow in obtaining recognition. Its first extended application<sup>5</sup> began at the Maryland Steel Works in 1907 for the purification of steel and it was used for the treatment of cast iron at the Carwheel Foundry of the Norfolk and Western Railway at Roanoke, Virginia, in 1908.

One of the first uses proposed for titanium compounds was the suggestion in 1846 that the pigment titaniumcyanide be substituted for the poisonous arsenical copper green then in common use in 1846. Despite this early suggestion, its use as a pigment was neglected for a long time until about 1910. Since that time considerable research has been done to produce titanium pigments for the paint industry, and today this field represents the most important use of titanium.

#### Physical and Chemical Properties

Titanium belongs to the same chemical group of elements as silicon, zirconium, cerium, and thorium. It resembles these in being quadrivalent with a lower valence in some cases; like zirconium, it may behave either as a weak base-forming or weak acid-forming element. In a general way its chemical properties are similar to those of silicon, but it differs from that element in that it is more active in its combining qualities and more energetic in its action. Metallic titanium, as prepared in the laboratory, does not differ in outward appearance from polished steel. It is hard and brittle when cold, and breaks with a steely fracture; but it is malleable at a low red heat and at that temperature may be readily forged like red hot iron. Its atomic

weight is 47.90 and the specific gravity 4.5. Hunter<sup>6</sup> determined the melting point as being between 1800° C. and 1850° C.

When heated in air it burns with extreme brilliance, hence has been used in fireworks. Titanium does not decompose water at ordinary temperatures, and acts but slightly on heated water. It is soluble in cold dilute sulphuric acid, in aqua regia, and hot concentrated hydrochloric acid, and more slowly in nitric acid; hydrofluoric acids also attack it. At 800° C. it combines quickly with nitrogen burning with incandescence to nitrates. Roberts-Austen<sup>7</sup> states that this is the only instance of vivid combustion of an element in nitrogen.

The compounds of titanium vary widely in their state of aggregation -- from the extraordinarily infusible cyanonitride<sup>8,9</sup>, to the fluid chloride, and the volatile hydrofluoride. Typical compounds are:

Oxides:  $TiO$ ,  $Ti_3O_4$ ,  $Ti_2O_3$ ,  $Ti_7O_{12}$ ,  $TiO_2$ ,  $Ti_2O_5$ ,  $TiO_3$ .  
 Hydroxides:  $Ti(OH)_4$ ,  $Ti(OH)_6$ .  
 Chlorides:  $TiCl_3$ ,  $TiCl_4$ .  
 Bromide:  $TiBr_4$ .  
 Iodide:  $TiI_4$ .  
 Fluoride:  $TiF_4$ .  
 Titanofluorides:  $R_2TiF_6$ , etc. (R = Fe, Al)  
 Sulphides:  $Ti_2S_5$ ,  $TiS_2$ .  
 Sulphates:  $Ti_2(SO_4)_3$ ,  $Ti(SO_4)_2$ .  
 Nitrides:  $Ti_3N_4$ ,  $Ti_5N_6$ ,  $TiN_2$ .  
 Carbide:  $TiC$ .  
 Silicide:  $TiSi$ .  
 Titanates:  $RTiO_3$ ,  $R_2TiO_3$ .  
 Acids: (see Hydroxides)  $H_2TiO_3$ .

Most important oxides are the dioxide  $TiO_2$ , the sesquioxide  $Ti_2O_3$ , and the peroxide  $TiO_3$ . The monoxide  $TiO$  has been prepared, but the existence of some of the others is doubtful. Titanium dioxide occurs in nature as three different minerals; rutile, brookite and anatase. It is one of the most stable compounds known. The pure white titanium oxide is widely used as a titanium pigment in paints and enamels.

Titanium forms only one stable carbide  $TiC$ , which is harder than carborundum. Ferro and Ferrocobalt compounds are used in making steel to prevent blow holes and to increase soundness because of their affinity for nitrogen and oxygen. Titanium chloride and titanium sulphate are used in the dyeing industry to remove color.

#### Titanium Minerals

A considerable number of titanium bearing minerals<sup>1,9,10</sup> are found, but only a few occur under conditions that entitle them to be classed as possible ores of titanium. Probably the only actual commercial ores are rutile and ilmenite. Some of the properties of the more important minerals are as follows:

Rutile. -- ( $TiO_2$ ) 60 per cent  $Ti$ , crystallized tetragonally, has hardness of 6 to 6.5; a specific gravity of 4.24 to 4.26. Its cleavage is fair in two directions and it has a sub-conchoidal fracture. It is usually reddish brown, but may be yellow, yellowish brown, or nearly black, and occasionally white or green. It is transparent to opaque and has metallic to adamantine luster.

It is insoluble in acids, but readily attacked by fused alkali-metal salts, and is then insoluble. Iron and vanadium to the extent of 1 or 2 per cent or even 10 per cent are often present. The rutiles of the higher iron content are jet black and are known as nigrine.

Rutile occurs in igneous, metamorphic and sedimentary rocks. Lindgren classifies it as one of the persistent minerals, that is, one formed under all conditions from those obtaining at great depth to those nearer the surface. It is ordinarily a very stable mineral, but, according to Van Hise under certain circumstances it alters to hematite, ilmenite, and sphene.

Common mineral associates are quartz, kyanite, magnetite, and ilmenite. In alluvial and water-sorted sands, rutile is accompanied by such heavy resistant minerals as ilmenite, magnetite, chromite, monazite, garnet, zircon, and spinel.

## Titanium Minerals (Continued)

Ilmenite. -- The formula usually given is  $\text{FeO.TiO}_2$  which carries 52.7 per cent  $\text{TiO}_2$  or 31.6 per cent Ti. Hardness is 5 to 6; specific gravity 4.5 to 5. Crystallizes in hexagonal system, as rhombohedra, but seldom found in distinct crystals. It is opaque black, with a sub-metallic luster, conchoidal fracture and a black or dark brown streak. It may be slightly magnetic, but is seldom appreciably so by ordinary tests.

Dana says that the ratio of titanium to iron varies widely, and includes a number of compounds intermediate between rutile and hematite (collectively called titanitic iron.) The variation is probably due either to molecular or to microscopic intergrowths of arizonite, geikialite, prophanite, hematite, and magnetite.

Ilmenite is difficultly soluble in acids, but decomposes slowly in hot hydrochloric or sulphuric acid.

Brookite. -- ( $\text{TiO}_2$ ) Crystallizes in orthorhombic forms, usually in thin tabular crystals. Hardness, 5.5 to 6; specific gravity 3.87 to 4.01; colors and other characteristics as in rutile.

Octahedrite. -- Sometimes called "anatase," is also  $\text{TiO}_2$ . Crystallization tetragonal, but usually in octahedrons. Hardness 5.5 to 6; specific gravity, 3.8 to 3.95; color, brown, indigo blue, black; otherwise like rutile

Arizonite. -- ( $\text{Fe}_2\text{O}_3. \text{TiO}_2$ ) Carries 60 per cent  $\text{TiO}_2$ . Has been recently recognized as forming the larger part of some sands classed as ilmenites, particularly those of Guilon and Cape Dakar (Senegal.) Its color is dark steel grey with some metallic luster; streak, brown; transparent, deep red in thin sections.

Sphene or Titanite. -- ( $\text{CaO.TiO}_2.\text{SiO}_2$ ) and Perovskite, ( $\text{CaO.TiO}_2$ ). May conceivably become useful titanium minerals, but no known bodies are large enough to allow possible exploitation.

Geikialite. -- ( $\text{MgO.TiO}_2$ ) and pyrophanite, ( $\text{MnO.TiO}_2$ ) are known separately only as mineralogical curiosities and are worthy of mention only because, as already noted, they form intergrowths with ilmenite.

General Geological Relations<sup>1,9,10</sup>

Titanium<sup>1,2</sup> is one of the more abundant elements. It ranks ninth in relative abundance of the ninety-two elements and has a very wide geologic distribution. But, unlike the common useful metals, a very small proportion of the aggregate bulk contained in the earth's crust is found concentrated in separate deposits. The greater proportion of it occurs diffused through such a vast amount of rock that its recovery is economically hopeless. There are enough concentrations, however, to make the available supply far in excess of any present or prospective demand.

Titanium minerals are found as minor accessories in all classes of rock--igneous, metamorphic and sedimentary. In igneous rocks they occur in the phases lowest in silicon and richest in iron. Igneous rocks high in calcium and potassium seldom contain much titanium.

By far the greatest quantity of ilmenite occurs as small dispersed grains or masses distributed in: (a) highly metamorphosed deep-seated rocks such as the schists and gneisses (b) andesites and more basic lavas and (c) in the gabbros and more basic rocks granular rocks. Of these the rocks of the gabbro family--anorthosites, norites and gabbros contain the most important ore bodies.

The ore bodies consist of aggregates of magnetite and ilmenite in various proportions. They occur as segregated masses whose boundaries grade into the country rock, as more sharply outlined streaks and as sharply defined tabular dikes and sills. It is possible to divide them into two groups; one associated with anorthosites or feldspar-rich gabbro and the other with normal gabbro as the country rock. The ores of the first group are as a rule coarser grained and contain little gangue. They include the largest ore bodies. Those of the second group are finer grained, contain much gangue, and are usually small and irregular in extent.

High grade mineable primary deposits of pure ilmenite are found only in a peculiar rock known as nelsonite in which ilmenite and apatite or rutile and apatite are the essential minerals. The origin of nelsonite bodies is not understood, although they have the form of dikes and seem to be of igneous origin. Apatite appears to have been the primary mineral in the bodies and to have been replaced by ilmenite or rutile until in some places only small pellets of apatite are left.

The known large deposits of rutile are found in pegmatites or in closely related basic rocks such as krageroite, a rutile plagioclase rock. The rutile occurs in minute crystals in some of the dark micas and in larger crystals in quartz veins closely related to the pegmatites. Like all primary titanium minerals rutile is believed to be of deep-seated origin.

Both rutile and ilmenite are extremely stable and resistant so that concentrations of "black sands" on streams and beaches as the result of weathering and erosion are common. Ilmenite placers are much more common than those of rutile. The concentration on some beaches is remarkably high, those of Travencore, India, and New South Wales, Australia, having 75 per cent or even more of the black sand as ilmenite, rutile, and zircon. Placer deposits are easy and cheap to work and furnish the great bulk of the world's titanium.

#### Origin of Deposits

Most economic titanium deposits<sup>11,12,13</sup> have been considered as magmatic segregations, and are found either in or closely associated with eruptive rocks of the gabbro family. There is considerable doubt, however, whether this origin holds for all, or even most, titanium deposits. The injected character of such deposits as those of Iron Mountain, Wyoming, has been generally accepted. In a study of the deposits of the Adirondack Mountains, New York, and those of Quebec, Canada, Osborne<sup>12</sup> recognized as magmatic injections only those deposits which were either concordant or discordant to the primary structure of the host rock.

Placer deposits of black sands are the result of mechanical processes of concentration.

RESOURCES AND PRODUCTION OF TITANIUM

World Commercial Resources and Production 1, 9, 14, 15

Titanium is very plentiful in the earth's crust and is a constituent of almost all common rocks; hence, titanium is found throughout the world. Ilmenite and rutile, however, are the only minerals extensively mined as titanium ores. Commercial deposits of these minerals are relatively few. The British Empire (British India and Canada,) Norway, Japan, and the United States have large resources of titanium and are thus independent. It is probable that France and Russia have enough resources to be self-sufficient.

A brief description of the world's titanium resources by countries is given below.

British Empire

British India. -- The famous Travancore deposit on the west side of the Indian Peninsula is the most productive ilmenite beach deposit in the world. As black sands on ocean beaches now supply about half the ilmenite consumed, it is by far the world's largest producer of titanium minerals. There are two strips of the Travancore coast that are productive; one in the southern part of the state, at Manavalakurichi, and the other 80 miles north, about 4 miles from the town of Guilon. The beach at Manavalakurichi was worked from 1911 to 1924 for monazite only, but then ilmenite was also produced and up to 1934 nearly all the production came from this beach. The reserve there has been largely depleted. The deposits north of Guilon, which run when concentrated from 59 to nearly 61 per cent  $TiO_2$ , are still large producers and have considerable reserves.

The production of ilmenite from these deposits has risen from 641 long tons in 1924 to over 129,000 long tons in 1936; the total production being over 700,000 long tons.



Canada. -- The best known titanium deposits of Canada are those near St. Urbain near Baie St. Paul, Quebec. From here about 2,000 tons of ilmenite ore carrying 35 to 40 per cent  $TiO_2$  have been shipped annually to Niagara Falls, New York for the manufacture of ferrocen titanium. The most important Canadian occurrences in point of probable size are: ilmenite deposits at St. Urbain, and at Ivry, in Quebec; titaniferous magnetite deposits near Lake St. John, Quebec; those at Bay of Seven Islands, Quebec, and an extensive series found along the shores of Seine Bay and Bad Vermilion Lake in Western Ontario. It is thought that all these deposits have considerable magnitude. Other known Canadian deposits<sup>1</sup> include one in Alberta; and a number of smaller ones in Ontario and Quebec. All are magmatic segregations genetically connected with basic eruptive rocks. It is highly probable that further prospecting will disclose additional Canadian deposits.

Australia. -- Several titanium occurrences of commercial quantity have been noted in Australia, but there has been little commercial production. In south Australia a small rutile deposit was formerly mined 15 miles east of Gawler. It is probable that the zircon, ilmenite, rutile placers of the northern coast of New South Wales will become active producers of rutile as a by-product of zircon. There are important beach deposits in Tasmania which are at present the important Australian producers. In 1933 Australia produced 569 metric tons of ilmenite.

Brazil. -- Brazil has large beach deposits of mixed ilmenite, zircon, and monazite along the coast of Espirito Santo, Rio de Janeiro and Bahia. In 1929 over 6,000 tons were exported, but, probably due to the competition of the Travancore deposits, the workings are now inactive. However, the very large quantity of ilmenite on the Brazilian beaches will in time be concentrated and exported. Some rutile is found associated with the diamond bearing gravels of Diamantina and 287 metric tons of rutile were produced in 1935.

Federated Malay States. -- Ilmenite is found in considerable quantities in the tailings from the cassiterite placers. It is estimated that large tonnages are available as a cheap by-product, costing only \$1.00 to \$2.00 per long ton loaded on ship board. In 1935 Malay produced 2,540 metric tons of ilmenite.

Japan. -- Japan has great quantities of black magnetic sand which is titaniferous. These sands are found on most beaches of Japan; the most concentrated sands being on the east coast of Aomori and Iwate prefectures. The deposits are estimated officially to contain 10,000,000,000 tons carrying as mined 20 to 30 per cent iron and 8 to 12 per cent  $TiO_2$  and .01 to 0.6 per cent  $V_2O_5$ . The sand can be concentrated to 60 to 65 per cent  $TiO_2$ . At Kuji, one hundred miles from the north tip of the island, is another large deposit said to contain a minimum of 200 million tons. Several companies have started operations for making titanium white and producing ferrocyan titanium.

Norway. -- One of the largest and purest ilmenite-magnetite deposits reported is that of the Titan Company at Josing Fjord, Norway. The deposit is estimated to contain 30 million metric tons of ore above a hundred meters depth. After concentration the ore carries about 42 per cent  $TiO_2$ , and it is here that the titanium-white pigment industry was started. The National Lead Company, of New York, now controls this deposit. Another deposit close by, the Laxedlas, contains about 250,000 metric tons of ilmenite-magnetite running 35 per cent  $TiO_2$ . In 1936 Norway produced 37,984 metric tons of ilmenite and 124 metric tons of rutile.

Portugal. -- A few hundred tons of ilmenite are mined in Portugal each year.

U. S. A. -- The titanium resources of the United States will be treated fully in the next chapter.

U. S. S. R. -- Russia, aside from the Scandinavian peninsula, possesses all the important titanium deposits of Europe. The largest reported is in the Ilmen Mountains, a branch of the Urals, where a deposit supposedly containing 400,000,000 tons of ore carrying 15 per cent  $TiO_2$  is located. Large deposits are also reported near Khibine, on the Cola Peninsula and at Gatskavo in the Ukraine. In 1936 prospecting was carried on at the Selianka mine in the Chelyabinsk. No production figures are available from Russia.

There are numerous other titanium deposits found throughout the world, but they are of minor importance and will not be discussed here.

#### World Production

15, 14

The world's production of titanium minerals as shown in Table I

Table I.--World Production of Titanium Minerals in Metric Tons, 1931-1936<sup>1</sup>

Mineral and Country	Approx. % Cont. $TiO_2$ per cent	1931	1932	1933	1934	1935	1936
<b>Ilmenite:</b>							
Australia (Tasmania).....				559.....			(2)
Canada (Quebec).....	18-25.....	1,369.....			1,835.....	2,076.....	2,528
Egypt.....	(2).....		487.....		164.....	183.....	(2)
French West Africa <sup>3</sup> (Senegal).....	47.....	370.....		160.....	540.....	1,250.....	(2)
British India (Travancore).....	54.....	36,746.....	50,856.....	53,830.....	76,858.....	129,090.....	(2)
Federated Malay States <sup>3</sup> .....	(2).....	(2).....	(2).....	204.....	51.....	2,540.....	(2)
Norway.....	44.....	5,000.....	13,481.....	23,213.....	26,306.....	37,984.....	(2)
Portugal.....	50.....	152.....	766.....	645.....	434.....	264.....	(2)
Sierra Leone.....	(2).....	10.....				(2).....	(2)
United States.....	(4).....	(4).....	(4).....	(4).....	(4).....	(4).....	(4)
<b>Rutile:</b>							
Brazil <sup>3</sup> .....			35.....	96.....	116.....	287.....	(2)
Cameroun, French <sup>3</sup> .....						45.....	(2)
Norway.....	90-95.....	21 <sup>5</sup> .....	30 <sup>5</sup> .....	56 <sup>5</sup> .....	247.....	124 <sup>5</sup> .....	(2)
United States.....		(4).....	(4).....	(4).....	(4).....	(4).....	(4)

1. Compiled by Miss M. T. Latus, U.S. Bureau of Mines.

2. Data not available.

3. Exports.

4. Bureau of Mines not at liberty to publish figures.

5. Concentrates.

6. G. A. Roush, *The Mineral Industry During 1936*, p. 663

McGraw-Hill

5,9,14,15

United States Commercial Resources

The United States is fortunate in having several large deposits of titanium minerals. The better known and most important will be discussed here by areas.

The Appalachian region

Rutile. -- The largest rutile deposit known is found at Roseland, Va., where it occurs as a pegmatitic replacement of a peculiar aplite. The deposit is owned and operated by the American Rutile Company who have erected a new mill reported to have a capacity of 1,800 to 2,000 tons per year. They have also an older mill with an additional capacity of 500 to 600 tons of rutile per year. The rock mined averages 4 to 5 per cent each of rutile and ilmenite. On concentration it produces a rutile concentrate carrying 92 to 98 per cent  $TiO_2$ , and an ilmenite concentrate running about 50 per cent  $TiO_2$ .

Smaller occurrences of rutile have been found throughout the length of the Appalachians. Among those receiving attention have been some near Johnson Springs, Va., near Goldin, Va., and a deposit on Shooting Creek, North Carolina. So far these deposits have not proved profitable for mining.

Ilmenite. -- Large deposits of titaniferous iron ores occur in the Adirondacks as ore bodies of ilmenite-magnetite in the country rocks of the anorthosites, dark gabbro, or norite. It is claimed that they have proven reserves of over 100,000,000 tons of ore. At present the grade, 7 to 23 per cent  $TiO_2$ , has been found too lean to compete with the ilmenites now being marketed. Some of the ore has been used for making ferrotitanium, but within recent years no ore is known to have been mined.

In Amherst and Nelson Counties, Va., there are several nelsonite dikes large enough to be of real value as producers of ilmenite. The largest of these dikes now known is in Amherst County and is the property of the Southern Minerals Products Company, a subsidiary of the Vanadium Corporation of America. The dike mined is of considerable magnitude; having a width varying from 60 to 400 feet and a length of some 3,000 feet. At present only the decomposed rock has been quarried. The rock contains 18.5 per cent  $TiO_2$  and should yield about 42.5 per cent of concentrate. The gangue is almost wholly apatite and has been used for a number of years to make large quantities of calcium monophosphate for use in baking powder. It has been estimated that the deposit (considering it extends to a depth of 400 feet) contains nearly 24,000,000 tons of nelsonite or more than 4,400,000 tons of  $TiO_2$ .

In the same two counties there are two other similar dikes which, although not thoroughly prospected, are said to carry 30 per cent  $TiO_2$  and probably contain at least 2,000,000 tons of ore or 600,000 tons of  $TiO_2$ . There are also many smaller dikes which might contribute an appreciable tonnage.

#### Minnesota

In northeastern Minnesota titaniferous magnetite is found occurring within an extensive area of the Duluth gabbro laccolith. These deposits have been known for over fifty years and those in the Iron Lake Region have received considerable study. The ore is believed to average about 11 per cent  $TiO_2$  and 49 per cent iron. The deposits are extensive, but to date have had little production.

#### Wyoming

Numerous bodies of titaniferous magnetite occur within the large pre-Cambrian anorthosite area of the Laramie Mountains, Albany County. Associated with the anorthosite are several gabbro masses either within it or along the contact. The best known deposits are those of Iron Mountain and of Shanton Ranch.

Iron Mountain. -- The Iron Mountain deposit outcrops along a ridge cut through by Chugwater Creek. The ore body has a width of from 50 to 200 feet and a length of over a mile. The ore averages about 51 per cent iron and 22 per cent  $TiO_2$  and consists of medium coarse grained magnetite and ilmenite with little visible gangue. The ore body has been considered by all except <sup>17</sup>Fowler to represent an intruded body, not a magmatic segregation.

Shanton Ranch. -- At Shanton Ranch several smaller dikes of magnetite-ilmenite occur similar to the Iron Mountain deposit. The deposits are believed to be injections in anorthosite. The ore has a titanium content as high as that of Iron Mountain. It contains a very small amount of gangue, mostly biotite.

#### Colorado

Caribou Hill. -- On Caribou Hill and Boulder County several ledges and pockets of titaniferous magnetite occur with small gabbro and pyroxenite masses in monzonites. The deposits are rather low grade, carrying only 2.5 to 4.5 per cent  $TiO_2$ , over a width of 50 to 100 feet and a length of 1500 feet.

Iron Mountain. -- A number of ore bodies are found on Iron Mountain in Fremont County associated with anorthosite or olivine gabbro. They vary in width from 10 to 50 feet and have sharp contacts with the wall rock. The average ore contains 48 per cent iron and 13 per cent  $TiO_2$ .

Cebollo Creek. -- An occurrence of titaniferous magnetite of unusual geological interest occurs on Cebollo Creek in Gunnison County. The ores occur as segregations in a pyroxenite and also in the contact metamorphic zone between intruded basic and alkaline igneous rocks and limestone. The ore occurs as a large number of small segregations consisting of aggregates of magnetite, ilmenite and bunches of dark brown mica. Analyses of the ore vary from 9 to 36 per cent  $TiO_2$ .

Arizona

Bureka mining district. -- A deposit occurs in Yavapai County which apparently is a magnetite rich phase of the gabbro averaging 61 per cent Fe and 15 per cent  $TiO_2$ . The gabbro consists of labrad<sup>or</sup>ite and pyroxene with magnetite, ilmenite, pyrite, and apatite as accessory minerals.

California

San Gabriel Mountains. -- The titaniferous iron ore of the San Gabriels in Los Angeles County are discussed in detail in Part II of this thesis.

Production of Titanium in the United States<sup>14,15</sup>

Due to the small number of producers involved, no statistics are published on the domestic output. The growth of the consuming industries must be judged largely by the imports which furnish the bulk of the supply of the raw material. The domestic production is apparently increasing somewhat, but not enough to supply to the present demand.

Table I United States Imports of Titanium (a)

Year.	Ilmenite.		Rutile.		Titanium and Ferrotitanium.		Titanium Potassium Oxalate, Etc.	
	Short Tons.	Value.	Short Tons.	Value.	Pounds.	Value.	Pounds	Value.
1931...	35,440	\$144,951	1	\$189	.....	.....	46,648	\$7,443
1932...	37,610	231,652	88	4,508	5,449	\$718	61,659	8,882
1933...	43,243	196,211	79	3,737	6,776	1,292	683,071	62,608
1934...	60,316	356,208	155	7,350	3,240	434	161,130	26,617
1935...	129,718	636,293	212	13,124	4,480	654	.....	.....
1936...	147,790	687,822	510	38,552	.....	.....	.....	.....

(a) Bureau of Foreign and Domestic Commerce.

<sup>9,15</sup>  
Prices. -- "Prices for titanium ores and products are evidently more or less nominal, as they remain unchanged throughout the year. The chief items, as listed in Metal and Mineral Markets, are as follows:

"Foreign ilmenite, 45-52 per cent, \$10 to \$12, per ton, f.o.b.

Atlantic seaboard; rutile, 94 per cent, 10c. per pound.

Ferrocobalt-titanium \$137.50 for 7-8 per cent C; \$142.50 for 3-5 per cent C.

Titanium metal, 96-98 per cent, \$6-\$7.

Titanium dioxide, 17c. per pound in paper bags, 17 1/4c. in barrels."

#### USES OF TITANIUM

1. Metallic alloys.--For metallurgical purposes<sup>1, 14, 17</sup> titanium is used in the form of ferro-titanium with a titanium content of 15 to 40 per cent. In the steel industry it is widely used as a scavenger for oxygen and nitrogen. It produces a flux with these elements which rises to the surface of the molten metal; producing a steel with oxide segregations reduced to a minimum. It is said to be better than aluminum for this purpose. Rail and structural steels especially are improved when treated with 0.1 to 0.25 per cent of titanium. In recent years there has been a great increase in the use of iron-titanium alloys in the steel industry for deep-stamping and automobile bodystock.

In the stainless steel industry the addition of titanium has been found to markedly improve the stainless qualities. For this purpose, the amount of titanium added to the steel must be at least 4 times the carbon content. By adding similar amounts of titanium to the high-chromium steels, important benefits were obtained. The titanium takes the carbon from the chromium and makes the steel more easily rolled when hot, prevents air hardening, makes it softer and more ductile after rolling and prevents intergranular corrosion. In the production of intermediate manganese steels, ferro-carbon-titanium is displacing more expensive alloys, notably nickel and vanadium.

In the nonferrous field several attempts have been made to use titanium alloys. When added to copper it forms an age hardening alloy of great strength. Other important developments have been the use of titanium in aluminum and in grey cast iron and the prospective use to assist in age hardening chrome-nickel steels. It is also found to be of value for addition to copper castings. These processes show promise and may become of importance commercially.



2. Incandescent Media.--The high fusion and vaporization points of titanium and its compounds coupled with efficient radiation has made titanium compounds useful in making electrodes for arc lamps. As early as 1878, Thomas A. Edison took out an English patent covering the use of titanium dioxide (rutile) in arc lamps. It was tried also in incandescent lamp filaments, but tungsten has proved to be better for this purpose. The addition of 33 per cent titanium to a nickel alloy with cobalt and iron produces an alloy known as "konel," which has been used in vacuum tube filaments. The alloy is useful for this purpose because of its great tensile strength at high temperatures. The field of incandescent media is, of course, limited and uses little titanium.

1,9  
3. Pigments.--Titanium has come into its own as an article of commerce mostly because it makes such an excellent pigment for paints. Titanium dioxide has a very high index of refraction and consequently reflects nearly all the light striking it, thus making it appear one of the whitest of pigments. Furthermore, the covering capacity of a pigment depends, among other things, on the numerical difference between the refracted index of the pigment and that of the binder used; and in this connection, it is interesting to note that if the refractive index of linseed oil be taken as unity then that of zinc oxide is 1.34, of white lead 1.36, of amorphous titanium dioxide 1.48, and of crystalline titanium dioxide 1.80. It is evident that titanium pigment has by far the highest difference in refractive index and consequently the greatest covering power of the paint pigments. Titanium dioxide has also the important advantage of being non-poisonous.

The making of pure white titanium dioxide from minerals is one of the most precise of chemical operations. It has taken competent staffs backed by ample financial and mechanical equipment, long periods to develop the technique. The process as developed is complex and is covered by hundreds of patents. Titanium pigments are now produced in England, France, Italy, Czechoslovakia, Norway, Germany, Russia, Australia, and Japan. The United States is still the principal producer and has four companies operating six factories.

Pigment is made as pure titanium oxide, as titanium oxide and barium sulphate, and as intimate mixtures of titanium oxide and calcium sulphate. It is used in nearly all American makes of enamel paints for inside use and to replace part of the other pigments in most good, ready mixed, outside house paint. There are several less important uses which help make the production of titanium-white pigments a growing business. In less than a decade it has grown from an insignificant industry requiring only 2 or 3000 tons of ilmenite to a large business whose needs now exceed 100,000 tons a year.

4. Ceramics.<sup>1,9</sup>---Titanium has been used in the ceramic industry for a long time, (until recently this was its principal use) and its consumption here has shown healthy growth. Titanium dioxide is used in ceramic glasses, in topaz yellow glass-ware, and to increase fluidity of acid-resisting enamels. For acid-resisting enamels as much as 8 per cent  $TiO_2$  is added, the yellow colorization being suppressed by a 2 per cent addition of sodium fluosilicate.

5. Welding.<sup>1,14</sup>---Rutile has proved itself very useful as the coating material on welding rods. It has been found that it stabilizes the arc used in electric welding and causes a much more homogeneous and pure weld metal to deposit. In 1935 it was estimated that at least 1200 tons of rutile were used on welding rods.

6. Miscellaneous Uses.<sup>1,9,14</sup>---Miscellaneous uses of titanium compounds are: As smoke screens and sky writing in the form of titanium tetrachloride, toilet preparations such as face powders, creams, soap, and other cosmetics. In addition, titanium pigments are being used to an increasing extent in paper, linoleum, in artificial silk (to remove luster,) in printing ink, white rubber, plastics, shoe polishes, for various leather and synthetic finishes, in dyeing and tanning, and as abrasives.

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IntroductionLocation.

The location and principal means of access to the deposits are shown on the maps, Plate # 1 and Plate # 2. The deposits occur in Los Angeles County, California, and are restricted to a belt between Sand Canyon and the headwaters of the Tujunga River.

Topography.

The surface is in general very rugged and deeply dissected by a net-work of steep-sided V-shaped canyons which range in depth from a few hundred to several thousand feet (see Plate # 2). The mountains range from 4,000 to 8,000 feet in altitude and are covered for the most part with thickets of dense manzanita. Water is found in the bottom of some of the canyons during most of the year. Good outcrops of the bedrock are found on the canyon sides or along road cuts over most of the area.

General Geology.

The general geology of the region has been described by William J. Miller<sup>1</sup> in the following manner: "The San Gabriel Mountains may, in a general way, be looked upon as a great block of pre-Cretaceous metamorphic and igneous rocks, thousands of feet high, bordered on all sides by Tertiary and quaternary deposits. The great block is clearly a horst, its mass broken into many minor blocks. It was uplifted to its present height in Quaternary time. There are three great bounding faults or fault zones: the Sierra Madre on the south, the San Andreas on the northeast, and the Soledad on the northwest.

The oldest set of rocks is made up of schists, crystalline limestones, and quartzites of pre-Cretaceous age (probably pre-Cambrian). This old sedimentary series, more or less associated with amphibolites, has been invaded in turn by bodies of hornblende-rich diorite, granite, anorthosite, diorite, quartz syenite, and granodiorite. Large areas of mixed rocks consist of schist or amphibolite

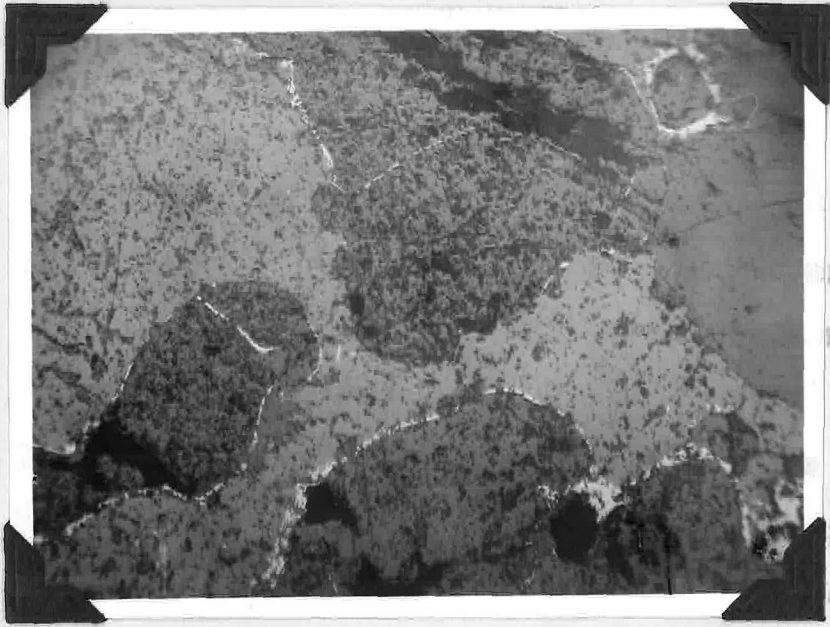


Fig. 2 - (Specimen R 3 51). Polished section showing formation of second generation magnetite from olivine. Mag. X 65



Fig. 3 - (Specimen 6 B 10). Polished section showing large grain of ilmenite (light) and the intimate intergrowth of the gangue with it. Mag. X 65

THE OREMineralogy -

Mineralogy of the deposits is relatively simple. Magnetite and ilmenite are by far the most abundant ore minerals and are the only ones of commercial importance. In addition, minor amounts of hematite, limonite, pyrite, molybdenite and rutile are present, as well as several abundant gangue minerals, described later. Following is a description of the minerals encountered:

(a) Metalliferous

Magnetite ( $Fe_3O_4$ ) was found in all the samples studied. There are two generations of magnetite present; one primary and the other forming as an alteration product from olivine. (See Fig. 2)

In the hand specimens it is difficult to tell magnetite from ilmenite. The appearance of the two ores under a hand lens is practically the same; both are heavy, have a grey-black color and a metallic luster. There is nearly always enough iron in the ore to give a characteristic brown stain to the rock; the amount of this stain is a very poor criterion of the amount of magnetite present. By means of a magnet it is possible to distinguish large differences in magnetite content, but this method is neither sensitive nor reliable. In polished sections magnetite and ilmenite also have similar properties. Both are grey, have nearly the same hardness and react negatively to all reagents. There is a slight color difference between the two minerals which can sometimes be noticed when the two are in contact, but by far the most useful distinguishing property is their behaviour under polarized light. Ilmenite, being hexagonal, is anisotropic, showing light brown and grey polarization colors, whereas magnetite is isometric and hence isotropic. This fact makes it possible to separate the minerals by visual inspection under polarized light.

Many attempts were made to find a method of differentially staining magnetite-ilmenite. Although some success was obtained by the use of hydrochloric acid mixed in alcohol, results on the whole were most unsuccessful.



Fig. 4 - (Specimen Iron Sand). Thin section showing an "actinolite" type ore rich in feldspar (white).

Mag. X 10.

Ilmenite ( $\text{FeO}$ ,  $\text{TiO}_2$ ) - Ilmenite is the only mineral of economic importance found in the ore. It, like magnetite, is present in all specimens studied. As stated above, the best way found to distinguish ilmenite from magnetite is by its behavior under polarized light. Commonly, the ilmenite is intergrown with magnetite and gangue. (See Fig. 3). For percentage of metallics and the ratio of magnetite to ilmenite in the ores see Tables IV and V.

Pyrite ( $\text{FeS}_2$ ) - A few grains of pyrite are noted.

Hematite ( $\text{Fe}_2\text{O}_3$ ) - Minor amounts of hematite are found in some of the sections studied. The mineral is not common, but some sections (R S 52 and R S 50) contain up to 1 per cent.

Limonite ( $\text{Fe}_2\text{O}_3$ ,  $\text{H}_2\text{O}$ ) - A coating of limonite is found on some of the weathered specimens.

Molybdenite ( $\text{MoS}_2$ ) - In some of the sections, particularly those of the Rattlesnake Group, several grains of molybdenite are found. Although the grains are small they display the characteristic four extinctions per revolution and are negative to all reagents. This mineral is of minor importance, but as much as 1 per cent is found in sections R S 50 and R S 52.

(b) Gangue minerals - Many gangue minerals are found intermixed with the ore. The most important of those noted include:

Feldspar - Feldspar is abundant and is found not only in the country rock, but also intimately mixed with the metallic minerals (See Fig. 4). It is commonly found intergrown with the magnetite and ilmenite, particularly in the Yerba Buena and Iron Mountain ores where the masses of magnetite and ilmenite are crowded with small inclusions of feldspar and other gangue. Two generations of feldspar are often present; the earlier is altered and contains many inclusions of magnetite, while the later is fresh and almost free from inclusions. The feldspars are principally ~~part~~ calcic andesine and labradorite.



Olivine - Olivine is a common gangue mineral (See Fig. 11). It is often altered to magnetite and less commonly to brown iddingsite, serpentine and biotite. (See Fig. 2). Where the olivine is extensively altered there is an appreciable increase in the magnetite-ilmenite ratio (See Table V) showing olivine to be an important source of magnetite on alteration.

Augite - Up to 30 per cent of pale green augite is found in some of the ore. The most common alteration product from it is actinolite.

Apatite - As much as 50 per cent apatite is present in some of the sections (See Fig. 10). It is unusual to have such a large percentage of this mineral in a rock and it is possible that apatite may become a by-product valuable as a fertilizer.

Quartz - Some quartz is found in the diorite type ore, but it is not as abundant as casual inspection of the hand specimens seems to indicate. It seldom exceeds 2 per cent and is usually found as small grains in the reaction rim of a magnetite hornblende-feldspar mass. C. A. Dawson<sup>3</sup> gives the following explanation for the presence of the quartz in the rock. He postulates that at first there was just magnetite present as inclusions in the feldspar crystals and that reaction between the two minerals began with the formation of hornblende and quartz. The reaction continued until the magnetite was used up and there remained only quartz, hornblende and feldspar. Why this reaction should take place in only some of the grains is hard to explain, but it may be due to impurities in the magnetite.

Rutile - Occasional small specks of a gray (in reflected light) anisotropic mineral,<sup>4</sup> which was determined to be rutile, were found. These specks are small, uncommon and of no commercial importance.

Leucocoxene - Another alteration product of the ilmenite is leucocoxene. As ilmenite is, as a rule, little altered, leucocoxene is not common.

Hornblende - Green actinolitic hornblende and brown hornblende are common mafic minerals associated with the ore.

Other Gangue Minerals found include: - A fibrous tremolite, brown biotite, chlorite, green serpentine, spinel (as inclusion in the magnetite) and calcite.



Fig. 5 - (Specimen <sup>FROM</sup> Placer). Section showing Wiedmannstätten structure due to intergrowth of ilmenite (light blades) and magnetite. Mag. X 65.



Fig. 6 - (Specimen R S 51). Section showing large grain of magnetite-ilmenite pitted with inclusions of gangue. Mag. X 65.

Paragenesis -

It is thought the minerals were formed in the following order: Ilmenite, magnetite, gangue minerals, pyrite, molybdenite, hematite, limonite, rutile and calcite. Magnetite and ilmenite were early and probably crystallized contemporaneously with the cooling intrusive. Later hypogene solutions invaded the deposit and brought in hornblende, pyrite, biotite, apatite, ~~olivine, quartz~~ and feldspar.

Ilmenite - Ilmenite and magnetite were the first of the metals to crystallize out. They are sometimes found intergrown in Widemannstatten pattern indicating <sup>crystallization</sup> ~~contemporaneous deposition from solid solutions~~ (see Fig. 5). In the Yerba Buena series some specimens show the ilmenite as definitely earlier than all other minerals present. Here no magnetite-ilmenite growths are present. In fact, the two metals are seldom even in contact. This does not hold generally, however, and the bulk of the evidence shows that magnetite and ilmenite crystallize contemporaneously. There is some evidence found in specimens from Group 3, Sand Canyon region, (see Plate 2 for location) that there are two generations of ilmenite, one very early in the history of the rock and a later occurring with the intrusion of gangue minerals. The first generation ilmenite is generally in large crystals that contain many <sup>fragments of wall rock</sup> ~~inclusions of gangue~~; the later ilmenite usually occurs as veinlets or blades and does not contain very much gangue as inclusions.

Magnetite - The magnetite crystallized contemporaneously with the ilmenite, probably during crystallization of the intrusive (see Fig. 5). There are two generations of magnetite, one <sup>pre-intrusive</sup> ~~before the gangue~~ which is present as inclusions in it, and another <sup>with</sup> ~~subhedral crystals and vein-like masses~~ <sup>in it</sup> that are definitely <sup>intrusive</sup> ~~gangue~~ (see Fig. 5). There is little apparent textural difference between the primary and later magnetite, except the first contains many gangue inclusions while the second is almost free from them (see Fig. 6). In almost every case it is possible to trace the veinlets of secondary magnetite back to the remnants of an olivine crystal, thus showing that most, or perhaps even all the second generation of magnetite, is an alteration product of olivine.

Gangue Minerals  - Following the crystallization of magnetite and ilmenite other minerals in the intrusive crystallized out. These were principally the dark mafic minerals, ~~hornblende~~, brown biotite, olivine, and apatite. There was also important amounts of feldspar (either calcic andesine or labradorite), but no quartz. Later there was an intrusion of mineral bearing solutions which brought in additional hornblende, biotite, apatite, and feldspar. It was during this period that the second generation of ilmenite and magnetite was formed. Calcite, up to 10 per cent, is found in some sections. It is very late and is probably of secondary origin.

Pyrite - It is thought that the pyrite crystallized at nearly the same time as the hematite.

Molybdenite - Molybdenite formed early in the paragenesis of the minerals. Its age relation with pyrite is not shown.

Hematite - The hematite is definitely later than the ilmenite and magnetite and may be seen cutting them in several sections including specimens R 3 52 and 51. It is not a common mineral, however, and is probably of secondary origin.

Limonite - Limonite formed as an alteration product of magnetite and ilmenite. It is late in the paragenesis of the ore.

Rutile - Rutile is of secondary origin due to alteration of ilmenite. It is late in the order of formation.

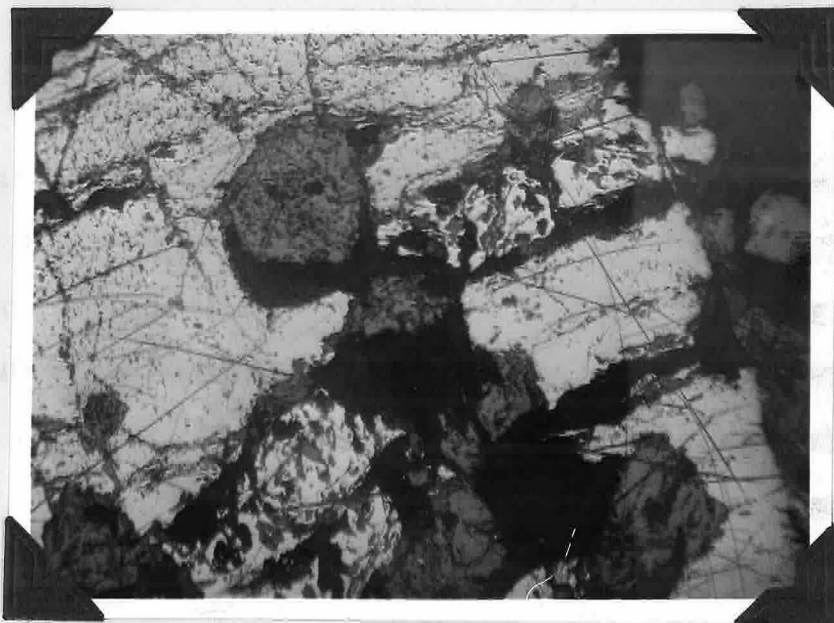


Fig. 7 - (Specimen F P C). Section showing an example of a rich coarse-grained magnetite-ilmenite ore of the "diorite" type. Mag. X 65.



Fig. 8 - (Specimen R S 52). Section showing the dispersion of the magnetite ilmenite grains among the gangue. A low grade specimen containing about 8 per cent metallics. Mag. X 65.

## Structures and Textures

A close study of the nature of the metallics within the ore is necessary. The mineral associations, amount of magnetite-ilmenite intergrowth, and grain-size largely determine the degree of grinding necessary to free the separate minerals and consequently vitally affect the hope of commercial separation of the ilmenite.

Almost all proportions of intergrowth between the magnetite and ilmenite are found. Sometimes the magnetite and ilmenite occur as separate grains, sometimes they are partially intergrown, and sometimes the two are so intimately mixed that it is impossible to separate them commercially. An interesting case of Wiedemannstatton structure due to magnetite-ilmenite intergrowth is shown in the Placer Specimen (Fig. 5).

Ilmenite is present in the ore <sup>as</sup> masses, small grains, blades, and thin veinlets. Its grain size ranges from less than .001 mm to 3.0 mm, with an average grain diameter of (0.9mm). The magnetite occurs as grains, thin veinlets and more rarely as large masses (see Fig. 7 and 8). It tends to be finer-grained than the ilmenite and has an average grain diameter of (0.75).

Tables III, IV, and V show the approximate grain diameters and the percentage of ilmenite that is estimated to be freed by different degrees of grinding.

The gangue minerals most closely associated with the magnetite-ilmenite are feldspar and hornblende. The secondary magnetite is in close conjunction with the olivine. Often the metallics are concentrated at the <sup>boarders of gangue grains.</sup> ~~intersection between grains of gangue.~~

The textures varied so from region to region (see Plate II) and even from one part of an ore deposit to another, that it is very hard to generalize regarding the textures of the entire deposit. For this reason it is desirable to present the following brief description of some of the sections studied.

R 3 51 - A dense, medium-grained "diorite" ore. The metallic minerals occur as large massive grains and constitute 40 per cent of the ore (see Fig. 6). They occur principally along gangue grain boundaries, but some occur within the gangue. Narrow veinlets of metallics cut the gangue crystals or outline their boundaries (similar to those shown in Fig. 8). There appears to be no difference in the grain size of the

ilmenite and magnetite. A small amount of the ilmenite occurs as blades in the magnetite oriented as if they were along cleavage or parting planes. Inclusions of gangue in the magnetite are larger and more numerous than those in the ilmenite. A few small grains of molybdenite were noted.

R # 52. - The magnetite and ilmenite occur as small grains, groups of grains or veinlets scattered throughout the section (see Fig. 8).

43 22 - Good ore, massive magnetite-ilmenite. Metallics occur as grains and clusters included in the feldspar gangue. Ilmenite grains are pure and contain practically no magnetite as intergrowths or inclusions.

43 31 - Section is mostly feldspar, but contains about 8 per cent metallics as dots and blades within the crystals and also as masses around the edges. The grains clustered at the crystal boundaries are composed of coarse grained ilmenite, practically free from magnetite.

53 7 - Much altered actinolite ore. Gangue is largely actinolite and feldspar. Magnetite-ilmenite present as dispersed grains containing abundant inclusions of gangue. Curved twinning planes in some of the ilmenite crystals showed they had suffered deformation. Some of the ilmenite and magnetite is scattered in such small specks throughout the gangue that it would be impossible to recover them commercially.

63 10 - Diorite type, large percentage of feldspar. Ilmenite makes up about 10 per cent of the rock. Only one grain of magnetite was noted. The ilmenite occurs as irregular grains which vary from submicroscopic up to 3 mm, about 90 per cent being 0.25 mm. Within the grains, however, are numerous gangue inclusions, which would require grinding to at least 0.10 mm to free (see Fig. 3). The ilmenite which is finer than 0.25 mm is present as small elongated grains oriented parallel to the feldspar cleavage or as fine graphic intergrowths of the feldspar and ilmenite. It is improbable that ilmenite finer than 0.25 mm can be economically recovered from this type of ore.

3D 5 - Massive ore, about 60 per cent magnetite and ilmenite with phenocrysts of feldspar

Both magnetite and ilmenite grains contain numerous gangue inclusions. Many magnetite crystals contain spinel. Wiedmannstätten intergrowths of magnetite-ilmenite are abundant.

FP 6 - Coarse-grained dioritic ore having 42 per cent metallics by volume, subdivided into 64 per cent ilmenite, 34 per cent magnetite and 1 per cent molybdenite. About 4 per cent of the ilmenite occurs as Wiedmannstätten intergrowths in the magnetite, and is too fine to separate. (See Fig. 7).

4B 8 - The metallic minerals (ilmenite 4 per cent; magnetite and hematite 3 per cent) comprise about 7 per cent of the rock. They are present both as disseminated grains and as veinlets in the gangue, particularly in the feldspar.



The ore may be conveniently classified into two main groups, the "diorite" type and the "actinolite" type. Although these groups do grade into one another and in the strictest sense do not include all the ore types, they are, nevertheless, distinct enough to serve in a useful field classification. It must be understood, however, that these are field names that have been found useful, not exact petrographic rock names.

"Diorite" type - In the hand specimen the diorite type appears to occur in a rock very like a grano-diorite, but on close examination under the microscope it proves to be a variety of gabbro (See Fig. 10). It is usually coarse grained with an average grain diameter of 0.5 mm. There are two generations of feldspar, one much altered and containing many inclusions, the other fresh with few inclusions. Both are calcic andesine or labradorite.

The quartz is probably of secondary origin and seems to be the result of alteration of the feldspar and hornblende. The ore bodies are of a disseminated character and are often found as stocks surrounded by the country rock. They are usually more resistant to weathering than the surrounding rock and hence outcrop as ridges. The diorite type of ore appears to be the most promising commercial source of titanium since it usually contains less magnetite than the other type of ore and is coarser grained. (Magnetite spoils the ore for the manufacture of pigment and must be removed before the ore can be treated).

An average composition for a diorite type of ore is:

Ilmenite.....	17 per cent
Magnetite.....	9 per cent
Feldspar.....	2 per cent
Apatite.....	30 per cent
Olivine and Augite.....	20 per cent
Quartz.....	1 per cent
Biotite, hornblende, rutile, chlorite, serpentine, leucocane, iddingsite.....	21 per cent

"Actinolite" type - The actinolite type is characterized by its lighter color, abundance of feldspar, and by the fact that the ore bodies usually occur as dikes

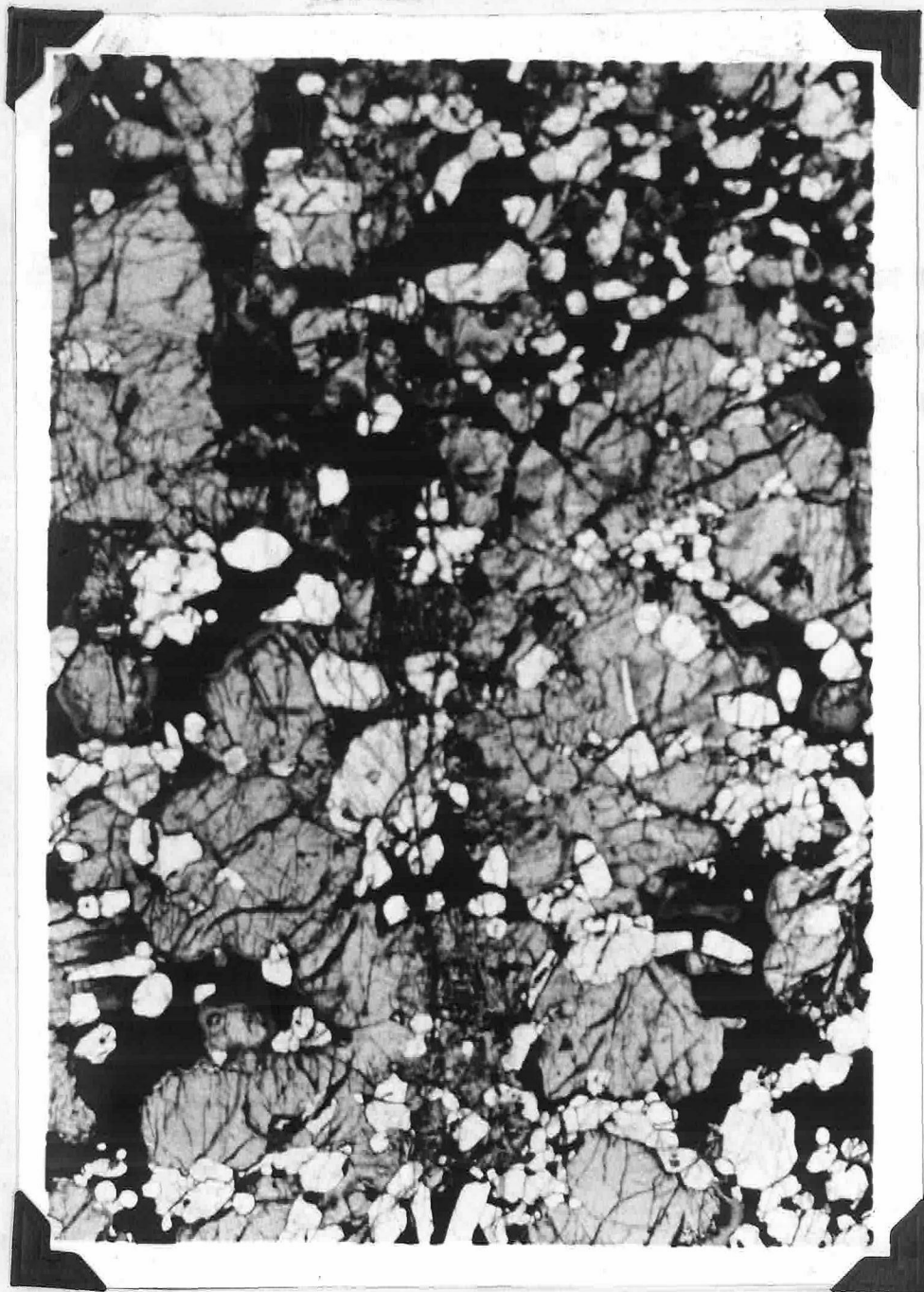


Fig. 9 - (Specimen R 3 55). Section showing "diorite" type of ore. Apatite (light), olivine and augite (grey), magnetite and ilmenite (black).

Mag. X 10.

or sills (see Fig. 10).

The following composition is representative:

Ilmenite .....	10 per cent
Magnetite .....	8 per cent
Feldspar .....	33 per cent
Olivine and augite.....	36 per cent
Apatite.....	7 per cent
Actinolite, chlorite, biotite, serpentine, rutile, leucocane, iddingsite, hematite.....	6 per cent

The actinolite is the softer of the two types and is less resistant to weathering. It usually contains a higher percentage of magnetite and hence is less desirable than the dioritic ore. Another objection is the metallies are finer grained, necessitating finer grinding and resulting in higher tailing losses.

### Form of Ore Bodies

As no underground work has been done on most of the ore bodies their true form is not definitely known. From an examination of the outcrops it appears that they occur as: (1) blebs or stocks surrounded by country rock, (2) sharply defined dike or sill-like masses, (3) less sharply defined streaks or schlieren, and (4) as irregular masses with gradational boundaries.

In the field it is often possible to distinguish the ore bodies because of the fact that they are physically stronger and more resistant to weathering than the surrounding rock. The durable magnetite-ilmenite float is abundant and often provides a valuable clue to the location of ore bodies.

### Secondary Enrichment

There has been little or no secondary enrichment at the San Gabriel titanium deposits. It is probable that the gangue minerals weather out before the magnetite-ilmenite, leaving them free to be carried away by erosion. They have not formed important placer deposits.

### Origin of the Primary Ore

It is believed that the primary ore of the San Gabriel titanium deposits was formed by magmatic segregation.

The San Gabriel mountains near San Fernando, where the ore deposits are located, have been invaded by one or more large gabbroic intrusions. Within this magma, it is thought that differentiation by crystallization caused the more basic materials, such as the iron and titanium minerals, to crystallize first, forming concentrations rich in magnetite and ilmenite. The magma was later eroded, exposing these concentrations of magnetite and ilmenite on the surface as the present ore bodies.

6,7,8,9

The following criteria suggest this as the true origin for many of the ore bodies:

- (1) The minerals of the ore are exclusively igneous rock-making minerals and their alteration products (see pages 25 and 26).
- (2) The texture of the ore is such that the minerals are intergrown like the minerals of an igneous rock; there is not crystallization as in veins.

(3) The size and shape of most of the ore bodies are suggestive of magmatic segregation. Deposits formed by magmatic segregation, like other igneous rock, may contain fragments of the rock invaded by the magma. This readily accounts for the irregular shape and inclusions of country rock in some of the ore bodies.

(4) The ore occurs in igneous rocks and must have cooled slowly to permit the formation of the Kiedmannst<sub>1</sub>ten intergrowths. In some sections, especially the Yerba Buena Series, there is evidence to show that the ore was formed, or at least enriched, by hydrothermal solutions. Several "diorite" ore bodies are located close to unaltered anorthosite rock, which although it is generally white in colour, does contain appreciable amounts of dark minerals. If the anorthosite rock were attacked by hypogene solutions bearing feldspar and dark mafic minerals, such as magnetite, ilmenite, apatite, biotite, and olivine, a rock very similar in composition to the "diorite" ore would probably result. The author believes this to be a reasonable explanation for the formation of the "diorite" ore as it is well recognized <sup>6,8</sup> that ores formed by magmatic segregation and ores deposited in and along fissures may be closely associated and closely related genetically.

### THE PROBLEM OF TREATMENT

Titanium ores are generally given a preliminary treatment to (1) improve the grade of the ore, and (2) to remove objectionable impurities such as magnetite or apatite. All iron in the ferric state must be removed or converted to the ferrous state before ilmenite may be treated to be made into a pigment for use in paint. As the conversion of ferric to ferrous iron is a costly chemical process, nearly complete separation of the magnetite from the ilmenite must be made in the mill before shipping. The presence of much apatite is objectionable as it lowers the grade of the ilmenite concentrate. One of the principal problems in connection with the San Gabriel deposits is whether or not the ore is amenable to treatment, i. e. is it possible to make a good ilmenite concentrate suitable for shipping and free from objectionable impurities, such as magnetite and apatite. To throw light on this problem many specimens were examined under the microscope to determine the nature of the ore. The following properties were especially noted: (1) the percentage of metallics present, (2) the percentage of ilmenite in the metallics, (3) the percentage of magnetite in the metallics, and (4) the approximate degree of grinding that would be necessary to free the metallics and to separate the magnetite from the ilmenite.

#### Mineragraphic Work

Polished sections may give much valuable information regarding the nature and texture of the ore. Samples are collected at the property, numbered and labeled as regards group and position and sent to the laboratory at the California Institute of Technology. Here the hand specimens are examined and suitable portions taken to be mounted for polished sections or made into thin sections. By correlating this work with grinding and milling tests carried out in the laboratory it is possible to: (1) decide on a rough plan of treatment, (2) estimate the degree of grinding necessary, and (3) have a rough check on the efficiency of the mill separation after a sample is tested.

Tables IV and V tabulate the results of the mineragraphic work.

The following table is used to convert the grain size determined under the microscope to screen sizes used in the milling laboratory.

Table 111

Wentworth Screen Scale (As Used In Tyler Screens)

Scale mm.	Mesh of Screen openings per sq. in.	Size of Opening in mm.
4	5	3.962
2	9	1.981
1	16	0.991
0.5	32	0.495
0.25	60	0.246
0.21	80	0.202
0.125	115	0.124
0.105	150	0.102
0.062	250	0.061

Following is a tabulation of some of the results obtained:  
**Table IV** POLISHED SECTIONS

Section No	Metallics % by wt.	Ilmenite % by wt.	Magnetite % by wt.	Ilmenite estimated to be freed by grinding to	
				-80 Mesh	-150 Mesh
<b>Group III - Sand Canyon Region</b>					
4 A 4	36	92	8		
4 A 5	8	80	20	50	80
4 A 9	10	82	18	75	90
5 B 6	8	80	20	80	95
4 B 2	10	70	30	90	96
4 B 8	11	58	42	70	86
4 B 18	8	75	25	75	85
4 B 19	13	80	20	95	99
4 B 22	22	90	10	60	90
4 B 26	20	60	40	90	98
4 B 31	8	75	25	70	85
5 B 2	16	60	40	80	95
5 B 7	14	90	10	75	85
6 B 4	23	85	15	80	95
6 B 10	16	100	0	90	97
3 C 3	19	83	17	65	83
4 C 3	20	90	10	70	90
4 C 6	19	75	25	80	90
4 C 8	23	80	20	60	75
2 D 2	18	70	30	80	90
2 D 9	16	90	10	55	80
3 D 1	10	50	50	70	90
3 D 6	30	60	40	90	94
4 D 1	33	55	45	75	90
8 E 1	18	90	10	80	90
Average	21	77	23	73	90
<b>Rattlesnake Canyon Region</b>					
R S 50	47	75	25	75	85
51	53	50	50	80	90
51A	29	70	30	75	85
52	8	70	30	70	85
53	47	65	35	75	85
54	13	70	30	65	85
55	47	60	40	85	95
F P C	42	65	35	90	98
S H	36	70	30	60	75
Average	36	66	34	75	87
<b>Iron Mountain</b>					
I M 27	20	91	9	85	95
28	24	94	6	95	100
29	27	80	20	80	93
30	15	88	12	65	80
31	22	89	12	90	97
32	24	90	10	75	90
33	27	94	6	80	95
Average	23	89	11	81	93
<b>Yerba Buena</b>					
Y B 1	26	85	15	83	96
3	37	84	16	93	98
5	25	86	12	96	99
7	24	92	8	94	97
9	27	83	17	78	97
11	24	94	6	90	97
13	30	75	25	75	90
Average	28	86	14	87	95



All percentages given in the table are by weight and are accurate to the nearest 5 per cent (although probably closer in most cases). The degree of grinding reported, 80 mesh and 150 mesh, is purely arbitrary and is used to show the average size of the grains and how much ilmenite should theoretically be unlocked if the ore is all ground to pass through screens of such fineness.

#### Summary of results

The Number 111 Group of claims, Sand Canyon Region, produced some exceptionally high grade samples, some as high as 88 per cent metallics by weight, but the average ore from this group is of much lower grade, averaging only 21 per cent metallics by weight. Of this percentage 77 per cent is ilmenite and 23 per cent is magnetite, and it is estimated that 75 per cent of the ilmenite is freed by grinding to pass on 80 mesh screen. (See Table 111).

That is to say, the polished sections studied indicate that it would be theoretically possible to obtain  $21 \times 0.77 \times 0.75 = 12$  per cent ilmenite or 240 pounds of ilmenite per ton of ore.

#### Samples from the Rattlesnake Canyon Region

(See Plate 11 for location) contained the highest percentage (36 per cent) of metallics of any group studied. The metallics have a magnetite-ilmenite ratio of 34.66 which is higher than the average and constitutes a serious disadvantage. On the average, 75 per cent of the ilmenite would be freed by grinding to 80 mesh.

Theoretically it should be possible to recover  $36 \times 0.66 \times 0.75 = 18$  per cent ilmenite or 360 pounds of ilmenite per ton of ore. This, of course, assumes a 100 per cent recovery of the ilmenite freed by grinding to 80 mesh and also that a clean concentrate free from both magnetite and gangue is obtained. In commercial treatment it is, of course, impossible to obtain such results.

#### Samples from the Iron Mountain Region

(See Plate 2) contain on the average 25 per cent metallics, with a low magnetite-ilmenite ratio of 11:89. This ratio is very favorable for concentration as it means there is almost nine times as much ilmenite as magnetite present.

It is theoretically possible to recover  $23 \times 0.89 \times 0.81 = 16$  per cent ilmenite or 320 pounds of ilmenite per ton of ore from these samples.

The last group of samples examined is from the Yerba Buena Series. They average 26 per cent metallics by weight and have a favorable magnetite-ilmenite ratio of 14:86. These specimens are the coarsest grained of the samples studied as 87 per cent of ilmenite is estimated to be freed by grinding to 80 mesh.

The theoretical recovery possible from this ore is  $26 \times 0.86 \times 0.87 = 19$  per cent ilmenite or 380 pounds of ilmenite per ton of ore.

A simple arithmetical means of the average of the four groups show the specimens to contain, on the average, 26 per cent metallics, of which 79 per cent is ilmenite and 21 per cent is magnetite. The grain size is such that 79 per cent of the ilmenite is freed by grinding to 80 mesh and 92 per cent by grinding to 150 mesh. (See Tables III and IV).

Theoretically it is possible to recover,  $26 \times 0.79 \times 0.79 = 16$  per cent ilmenite or 320 pounds of ilmenite per ton of ore by grinding it to 80 mesh. By grinding to 150 mesh the theoretical recovery would be increased to  $26 \times 0.79 \times 0.92 = 19$  per cent ilmenite or 380 pounds of ilmenite per ton of ore.

Again let it be understood that the above results are theoretical and are obtained from a relatively few samples. Hence while they do serve as a useful guide, the figures should not be considered as representative of the whole deposit in either grade or recovery.



FIG. 10 - (specimen R S 65). Thin section showing an ore rich in both apatite (white) and metallics, magnetite and ilmenite (black).

Mag. X 10.

A group of thin sections were studied to identify the non-opaque minerals and to determine their approximate abundance. The petrographic work also served as a valuable check on the polished section work. The mineral apatite, because of its possible value as a by-product was given special study. The thin sections showed that it is an abundant constituent of the ore and is often intimately mixed with the magnetite and ilmenite. (See Fig. 10).

In thin sections, besides the metallics, the following minerals were identified: Apatite, olivine, augite, feldspar, brown biotite, actinolitic hornblende, chlorite, brown hornblende, serpentine, and iddingsite.

Table V tabulates the results from the thin sections studied.

Table V THIN SECTIONS

Specimen Number	% Metallics	% of Total Non Metallics				% Apatite estimated to be freed by grinding to 80 mesh.
		Apatite	B	O	D	
<b>"Diorite" Ore (R S = Rattlesnake Group)</b>						
RS 55	24	37	00	59	4	98
RS 65	27	52	0	Alt.	48	96
RS 66a	26	45	0	55	2	98
RS 66b	26	37	0	Alt.	73	96
<b>Average</b>	<b>26</b>	<b>40</b>	<b>0</b>	<b>28</b>	<b>32</b>	<b>97</b>
<b>"Actinolite" Ore</b>						
RS74	12	3	45	40	4	40
RS75	6	4	60	30	2	50
Kath1	16	10	30	45	5	88
Kath2	19	15	10	60	15	90
Iron Sand	6	5	55	35	2	90
<b>Average</b>	<b>11</b>	<b>8</b>	<b>40</b>	<b>45</b>	<b>7</b>	<b>78</b>
<b>Grand Average</b>	<b>18</b>	<b>24</b>	<b>20</b>	<b>56</b>	<b>19</b>	<b>84</b>

B - Feldspar      O - Olivine and augite      D - All others      Alt. - Olivine has been nearly completely altered.

All percentages accurate to 5% or better. Percentage of non-ore minerals is by weight; all others by volume.

The minerals classed as "all others" are a brown biotite, actinolitic hornblende, apple-green chlorite, tremolite, greenish serpentine, brown hornblende, rutile and iddingsite.



Fig. 11 - (Specimen R B 66 b). Thin section showing almost complete alteration of olivine to magnetite and serpentine.

Mag. X 10.

Summary of Results:

The thin sections examined contained, on the average, 18 per cent of the ore minerals, magnetite and ilmenite. This is somewhat lower than the figure 26 per cent obtained from a study of polished sections. The reason for this is that specimens from a richer suite of ores were studied in polished sections. If the "diorite" ore specimens from Rattlesnake (R S) Group, which were studied in both thin and polished sections, are considered alone their average metallic content is found to be 26 per cent.

The sections (Kath 1, Kath. 2 etc) richest in olivine and augite are also low in metallics showing that olivine commonly alters to magnetite (See Fig. 11) thus increasing the magnetite-ilmenite ratio and at the same time the percentage of metallics.

Apatite on the average makes up 24 per cent of the volume of the non-metallic minerals or 18 per cent of the total weight of ore in the specimens studied. Grinding to 80 mesh frees 83 per cent of the apatite present. That is  $18 \times 0.83 = 15$  per cent apatite or 300 pounds of apatite per ton of ore may theoretically be recovered.

When it is realized that some of the ore contains 300 pounds of apatite and 320 pounds of ilmenite per ton, it is evident that some portions of the San Gabriel deposits well merit the development and study given to them.

Conclusions

1. (a) The ore of the San Gabriel titanium deposits contains the following minerals: ilmenite, magnetite, gangue minerals, pyrite, molybdenite, hematite, rutile, and limonite.
- (b) Magnetite and ilmenite are the only abundant metallic minerals and are the only ones of commercial importance.
- (c) The principal gangue minerals are: apatite, olivine, augite, hornblende, feldspar and biotite-mica.
2. The minerals are believed to have formed in the succession given in 1 (a).
3. (a) The primary ore of the San Gabriel titanium deposits was formed by magmatic segregation and is probably genetically related to the local gabbroic intrusive.
- (b) Some of the ore bodies were formed or later enriched by the action of hypogene solutions.

4. Microscopic work indicated that the magnetite-ilmenite ore would be amenable to separation. Suitable milling equipment must be found, however, to overcome the physical difficulties of separating the magnetite from the ilmenite.
5. The abundance of apatite indicates that it may become a by-product, valuable as a fertilizer.

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