

# Mineral Commodity Report 16 — Titanium

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## Discovery and Origin of Names

Titanium was discovered in 1791 by the British clergyman William Gregor while analysing black magnetic sand from Menachan in Cornwall. He produced a white metallic oxide from the mineral menachanite, a variety of ilmenite, and named the new element menachite. In 1795, the German chemist Martin Heinrich Klaproth realised that Gregor's description of the oxide coincided closely with the properties of an oxide that he had isolated from a sample of Hungarian rutile. Klaproth named the metallic element in the oxide titanium. Impure titanium was prepared by Nilson and Pettersson in 1887, however the pure metal was not isolated until 1910, when Mathew A. Hunter in the USA produced titanium by the reduction of titanium tetrachloride with sodium. The metal was a laboratory curiosity until Kroll, in 1946, showed that titanium could be produced commercially by reducing titanium tetrachloride with magnesium. By the mid-1950s, a number of Japanese and American companies were producing titanium in quantity by the Kroll method.

The name titanium is from the Greek *Titan*, one of a mythical race symbolic of brute force and large size. Ilmenite, the principal titanium ore mineral, was named from the Ilmen mountains in the south Urals.

## Major Ores and Minerals

Titanium ranks ninth in abundance among the elements in the earth's crust. It is found in practically all rocks and sediments, and is present in plants, animals and natural waters. Titanium is not found as a pure metal in nature; it is mainly in chemical combination with oxygen and occurs in some 60 minerals. The most important economic minerals are ilmenite  $FeTiO_3$  and the titanium dioxide minerals rutile, anatase and brookite, which although they all have the same formula, differ in their crystalline structure. Leucoxene is an oxidation product of ilmenite and is composed of finely crystalline rutile. Titanium is common in magnetite, with Ti-rich (2–20%) varieties termed titaniferous magnetite or titanomagnetite. Other less common titanium oxide-bearing minerals are pseudobrookite  $Fe_2TiO_5$ , perovskite  $CaTiO_3$ , geikielite  $(Mg,Fe)TiO_3$  and pyrophanite  $MnTiO_3$ . The only silicate mineral with titanium as a major component is titanite, formerly called sphene.

Ilmenite commonly occurs altered to mixtures of  $TiO_2$ ,  $FeO$  and  $Fe_2O_3$ , with the  $TiO_2$  content increasing from 49 to 75% as the mineral oxidises and iron is leached out by groundwater. Altered ilmenite (60–75%  $TiO_2$ ) is usually amorphous, but the leucoxene (76–90%  $TiO_2$ ) stage begins to show the definite crystalline structure of rutile. The name "pseudorutile" has been proposed for ilmenite alteration products containing

Symbol	Ti
Atomic no.	22
Atomic wt	47.88
Specific gravity	4.54
Valence	2, 3, 4
Melting point	1660°C
Boiling point	3287°C
Crustal abundance	0.62%
Preferred analysis method	x-ray fluorescence
Routine detection limit	10 ppm

75–92%  $TiO_2$ . The final alteration products show either rutile or anatase structure and contain 92%  $TiO_2$ .

## Properties

Titanium is one of the transition elements in Group IVB of the periodic table. Its chemistry shows many similarities to those of silicon and zirconium, although the aqueous solution chemistry shows some resemblance to those of vanadium and chromium. Titanium is a silver-white metallic element with a low density, good strength, excellent corrosion resistance, very low electrical and thermal conductivity, and is paramagnetic. Titanium is as strong as steel but 45% lighter. It is 60% heavier than aluminium, but twice as strong. Titanium has a lower coefficient of expansion and lower thermal conductivity than either steel or aluminium alloys. Pure titanium is malleable and ductile but it becomes brittle when contaminated with other elements such as carbon and nitrogen. It can be polished to a high lustre. Titanium is dimorphic. The hexagonal alpha form transforms to the cubic beta form at 883°C, although impurities may raise or lower this transition temperature. Natural titanium consists of five stable isotopes  $^{46}Ti$  (8%),  $^{47}Ti$  (7.3%),  $^{48}Ti$  (73.8%),  $^{49}Ti$  (5.5%) and  $^{50}Ti$  (5.4%). Several unstable isotopes are known.

Titanium has a strong affinity for oxygen, carbon and nitrogen, making it difficult to obtain in the pure state. It burns in air at about 1200°C and in oxygen at 610°C, and is the only element that burns in nitrogen, at about 800°C. It is soluble in hot water and in sulphuric and hydrofluoric acids, and insoluble in cold water.

The mineralogical properties of the main titanium minerals are summarised in Table 1.

## Formation

The geology of titanium mineral deposits was reviewed by Force (1991), and their world distribution was summarised by Towner *et al.* (1988). More than half of the world's

Name, Formula	% TiO <sub>2</sub>	Colour	Hardness	Density	Lustre	Crystal form	Transparency	Fracture
Ilmenite FeTiO <sub>3</sub>	52.6	black	5-6	4.5-5.0	submetallic	hexagonal	opaque	conchoidal
Perovskite CaTiO <sub>3</sub>	58	black, brown, reddish-brown or yellow	5.5	4.48-4.26		monoclinic (pseudocubic)		
Rutile, anatase, brookite TiO <sub>2</sub>	95	reddish-brown, red, yellowish or black	6.0-6.5 (rutile) 5.5-6.0 (anatase and brookite)	4.23-5.5 (rutile) 3.82-3.97 (anatase) 4.08-4.18 (brookite)	metallic or uneven	tetragonal (rutile, anatase) orthorhombic (brookite)	opaque or subtransparent	subconchoidal or uneven, brittle
Titanite (sphene) CaTiSiO <sub>5</sub>	35-40	brown, green, grey, yellow or black	5.0-5.5	3.45-3.55	adamantine or resinous	monoclinic	transparent to opaque	imperfect conchoidal, brittle

Table 1: Properties of some titanium minerals.

titanium production is from ilmenite and rutile in shoreline placer deposits in Australia, South Africa, the USA, India and Sri Lanka. Most of the remainder is supplied by magmatic ilmenite deposits in Canada, the Commonwealth of Independent States, Norway, Finland and the USA. A fluvial placer deposit in Sierra Leone has produced a substantial quantity of rutile. Future titanium ores may be produced from weathered magmatic deposits of anatase in Brazil or from perovskite deposits in the USA.

The magmatic deposits yield ilmenite with a TiO<sub>2</sub> content of 35–40%, whereas the shoreline placer deposits provide ilmenites of higher TiO<sub>2</sub> content, including altered ilmenite (60–75% TiO<sub>2</sub>), leucoxene (76–90% TiO<sub>2</sub>) and rutile (95% TiO<sub>2</sub>).

### Magmatic deposits

The most significant class of magmatic ilmenite deposits are associated with anorthosite or anorthosite-gabbro complexes, mostly of Precambrian age. The ores typically occur in ilmenite-rich lenses, dikes and sills cutting the anorthosites, and of lesser importance, disseminated in the anorthosites. The ilmenite probably crystallised from an immiscible iron-titanium-rich heavy liquid phase of a ferrodiorite magma (Force, 1991), which formed syngenetic layers and segregations, as well as autointrusions into partly or wholly solidified anorthosite-gabbro. Minerals include ilmenite, titaniferous magnetite (with exsolved titanhematite and ulvospinel), plagioclase, pyroxene, olivine, garnet, biotite, apatite, rutile and pyrrhotite. Deposits range from 1 to 300 Mt, containing 10–45% TiO<sub>2</sub>, 32–45% Fe and 0.2% or less V. Examples include Tellnes and Egersund in Norway; St. Urbain, Ivry, Lac Tio and St. Charles in Quebec; and the Kola Peninsula in the Commonwealth of Independent States. At Tellnes, the world's largest ilmenite deposit, anorthosite is intruded by an ilmenite-rich, norite orebody up to 2.7 km long, 400 m wide and 350 m

deep. Approximately 100 Mt of ore has been mined to date and remaining reserves are about 200 Mt containing 18% TiO<sub>2</sub>, 2% magnetite, and 0.25% pyrite and Cu-Ni sulphides.

In a second class of magmatic deposits, perovskite, rutile, brookite and/or ilmenite occur in alkaline ring complexes predominantly composed of nepheline syenites, but are particularly associated with pyroxenite phases. The titanium minerals mostly occur in magnetite-perovskite dikes intruding pyroxenite. Examples include the Ilmen Range of the Ural Mountains (type locality for ilmenite), the Powderhorn district in Colorado (perovskite), and Tapirá and Salitre in Minas Gerais State, and Catalão I in Goiás State, Brazil (anatase). Resources at Powderhorn are more than 500 Mt containing about 8% separable perovskite with 45–50% TiO<sub>2</sub>. Tapirá has reserves of 190 Mt of anatase ore containing 21.6% TiO<sub>2</sub> and produces anatase concentrate containing 91–92% TiO<sub>2</sub> in a 0.4 Mt/year plant. The presence of Nb, REE and Th in the oxide minerals of this class of deposit makes refining difficult and there is currently no commercially operating process for recovery of TiO<sub>2</sub> from perovskite.

Some alkaline anorthositic complexes have contact metasomatic deposits of rutile on their margins. Significant tonnages of rutile ore may be developed where swarms of anorthosite dikes and sills permeate country rocks, as in the Roseland District, Virginia (Force, 1991). Small deposits of rutile have also been found in some albitite aplite intrusives at Kragerø, in Norway and Beaver Creek in New York.

### Shoreline placer deposits

Heavy-mineral concentrations developed in coastal beach and dune sands provide most of the high-grade ilmenite, leucoxene and rutile used by industry. These placer deposits have formed in modern beach environments or are older

raised beach deposits formed during the Pleistocene. Economic beach placers are typically 10 m thick, 1 km wide and over 5 km long. The major producing countries are Australia, South Africa, the USA, India, Sri Lanka, Malaysia and Thailand. New deposits are being developed in Vietnam and Mozambique (Gambogi, 1997).

Rutile, along with zircon and ilmenite is mined from several Quaternary beach and dune heavy-mineral sand deposits along the east coast of Australia, from Tomago near Newcastle in the south, to North Stradbroke Island, near Brisbane (Wallis and Oakes, 1990). North of Stradbroke Island to Gladstone, the proportion of ilmenite increases at the expense of rutile and zircon. On the west coast of Australia, ilmenite, leucoxene, rutile, zircon and monazite are recovered from Pliocene and Quaternary shoreline deposits, mainly near Bunbury in the south and at Eneabba 225 km north of Perth (Baxter, 1990). Recently discovered ilmenite-leucoxene heavy mineral sand deposits on the southeastern margin of the Murray Basin in Victoria, are hosted in Pliocene marine sands (Williams, 1990). These deposits are very extensive, but are yet to be developed because of their low grade (average 2.8% heavy minerals) and fine grain size of the heavy minerals.

In South Africa, heavy-mineral deposits occur in Holocene high dunes at Richards Bay, about 160 km north of Durban. They are commonly about 20 m thick and average 10 to 14% heavy minerals. Ilmenite, rutile and zircon make up about 5.9% of the bulk ore.

In the USA, Pleistocene beach deposits in Jacksonville District, Florida (Trail Ridge and Green Cove Springs), produce ilmenite, a leucoxene-rutile mixture, and rutile, with zircon, staurolite and monazite as coproducts. Nearby modern beach deposits were mined in the past. The district has produced about 5 Mt of  $TiO_2$  and has resources of about 14 Mt. Deposits in New Jersey produced ilmenite during the 1970s and early 1980s. Undeveloped resources are known in Georgia, Tennessee and the Carolinas. India produces ilmenite and rutile from Holocene beach deposits near Quilon and Manavalakurichi on the southwestern coast. Large deposits have also been reported in the Chatrapur area. Malaysia and Thailand produce small quantities of titanium minerals as byproducts from shoreline placer tin mining.

### Alluvial placer deposits

Rutile has been mined from Quaternary alluvial deposits in the Gbangbama district of Sierra Leone, where the deposits are mostly about 10 m and up to 20 m thick, and lie directly on bedrock. They are radial to the Gbangbama Hills, which are composed of garnet amphibolites and garnet granulites, the latter containing 0.2 to greater than 1% rutile. Total heavy-mineral contents in the alluvial material commonly range from 1 to 5%, with rutile contents ranging from 0.5 to 2%. A rutile-rich source and weathering have been major factors in the development of the deposit. Titanium oxide minerals have also been produced as a byproduct of alluvial tin mining in Malaysia, Indonesia and Thailand.

## Uses

About 95% of titanium ore is processed into titanium dioxide, known as titanium white, a brilliant white, non-toxic pigment used as a whitening or opacifying agent in paints, lacquers, plastics, textiles, rubber, paper, glass, glazes and printing inks. It is supreme as a white pigment because of its chemical inertness, high whiteness, opacity, high refractive index, and light-scattering properties. Its opacity is twice that of zinc oxide and three times that of lead oxide.

Non-pigment uses of titanium ores are mostly in the production of titanium metal, but also include the production of various titanium compounds for industrial uses, the use of rutile in manufacturing welding rod fluxes, and the use of ilmenite in well-drilling mud and as a sandblasting abrasive.

Because of their high strength, light weight, and resistance to corrosion, titanium metal and titanium alloys are used in parts for aircraft, spacecraft, missiles and ships. The relative inertness of titanium makes it suitable as a replacement for bone and cartilage in surgery and as a pipe and tank lining in the processing of foods. It is used in heat exchangers in desalination plants because of its resistance to saltwater corrosion, which is better than stainless steel. In metallurgy, titanium alloys are used to remove oxygen and nitrogen from molten metals such as steel. Titanium is used as an alloying addition in many steels to reduce carbon content, in aluminium to refine grain size, and in copper to produce hardening. There are increasing applications of titanium in consumer goods such as golf club heads, and as body casings for high quality watches and cameras.

Titanium hydride  $TiH_2$  is used in powder metallurgy, in the production of hydrogen, as a getter in vacuum tubes, and in the production of foamed metals. Barium titanate  $BaTiO_3$  is widely used in the electronics industry because of its high dielectric constant. Organic alkali titanates are used as waterproofing agents. Titanium trioxide  $TiO_3$  is used in dental porcelain. Titanium tetrachloride  $TiCl_4$  is used to obtain titanium metal, for skywriting and producing smoke screens, as a catalyst in the polymerisation of ethylene, a mordant in the textile industry, in artificial pearls, and in titanium pigments. Titanium trichloride  $TiCl_3$  is used as a catalyst in the manufacture of polypropylene. Titanium nitride  $TiN$  is used in cermets and semiconductor devices. Titanous sulphate  $Ti_2(SO_4)_3$  is used as a reducing agent in the textile industry.

## Price

Ore prices are mainly fixed on contract and some large consumers have captive ore supplies. In late 1997, some prices quoted were A\$105-125 per tonne (t) FOB (freight on board) for Australian ilmenite bulk concentrate (54%  $TiO_2$ ), A\$480-550 per t FOB for West Australian bulk leucoxene (typically 91%  $TiO_2$ , maximum 1%  $ZrO_2$ ), and US\$500-550 per t FOB for Australian rutile bulk concentrate (95%  $TiO_2$ ). Crowson (1996) noted average 1995 prices of US\$300 per t FOB for Sorel Quebec slag (80%  $TiO_2$ ), US\$350 per t FOB for Richards Bay, South Africa slag (85%  $TiO_2$ ) and US\$3.97 per lb for sponge titanium metal.

## World Production and Consumption

Titanium is supplied to world markets mainly as ilmenite concentrate, rutile concentrate, synthetic rutile (92–94%  $\text{TiO}_2$ , derived after the iron has been leached from ilmenite) and titaniferous slag (75–85%  $\text{TiO}_2$ , derived from electrothermal smelting of ilmenite). In addition to these products, Adams (1994) noted that about 5% of the world's titanium minerals demand is met by low grade ilmenite (including titaniferous magnetite with up to 20%  $\text{TiO}_2$ ), which is used as a metallurgical flux or blast furnace additive. Small tonnages of leucoxene (87–91%  $\text{TiO}_2$ ) and anatase (90–95%  $\text{TiO}_2$ ) are also used, but these minerals currently represent less than 1% of global titanium minerals consumption. Perovskite, brookite, titanite and other titanium minerals are not commercially exploited at this time.

In 1995, the major producing regions of ilmenite concentrate were Australia (2.19 Mt), Norway (0.85 Mt), India (0.35 Mt) and USA (0.26 Mt), whereas the major rutile concentrate producers were Australia (0.32 Mt), South Africa (0.14 Mt) and USA (0.03 Mt) (Heap, 1996). Sierra Leone was also a major rutile producer (0.15 Mt in 1994), but production ceased in 1995 following invasion of Sierra Rutile's mine by rebels. The major producing regions of synthetic rutile in 1995 were Australia (0.59 Mt), USA (0.15 Mt) and India (0.09 Mt), whereas Canada (1.1 Mt), South Africa (0.95 Mt) and Norway (0.2 Mt) were the major titaniferous slag producers.

Production of pigment dominates the titanium industry and in 1995 the major pigment producing regions were the Americas (1.54 Mt), western Europe (1.28 Mt), Japan (0.3 Mt) and Australia (0.2 Mt) (Heap, 1996). Total world demand for pigment in 1995, was estimated at 3.34 Mt (Mining Journal, November 1, 1996, p. 358).

World reserves of ilmenite expressed in terms of contained  $\text{TiO}_2$  are estimated at 440 Mt, and identified resources total about 1,000 Mt (Crowson, 1996). The largest ilmenite reserves are in South Africa, Norway, Australia, Canada, India, China and Brazil. World reserves of rutile are about 165 Mt, of which 52% is in Brazil (mainly as anatase), and identified world resources total about 230 Mt (Crowson, 1996). Major reserves of rutile are also in South Africa, India, Sri Lanka and Australia.

## Ore Processing, Smelting and Refining

Ore from hard rock deposits is crushed to reduce the material to a size where the impurities are liberated. The titanium minerals are concentrated using magnetic separators or froth flotation. Heavy-mineral beach sands are typically mined with dredges and the heavy minerals are separated from quartz using gravity concentration (spirals, cones or sluices). The heavy-mineral concentrates are then fractionated using magnetic and high-tension separators (ilmenite and altered ilmenite are magnetic, whereas rutile is nonmagnetic).

There are two main methods of manufacturing titanium dioxide, the traditional sulphate process and the more modern chloride process that now accounts for more than 50% of production capacity. Each requires a different feedstock. In the sulphate process, ilmenite with 45–65%  $\text{TiO}_2$  or titanium slag with 70–72%  $\text{TiO}_2$ , is dissolved in sulphuric acid to form titanyl sulphate and ferrous sulphate. Titania is precipitated by hydrolysis, and is then filtered, washed, and calcined to produce  $\text{TiO}_2$ . This method has the disadvantage of producing substantial acidic wastes of ferrous sulphate, causing widespread environmental concern and criticism.

The chloride process requires a feedstock with a higher  $\text{TiO}_2$  content, such as rutile, synthetic rutile, or a slag with more than an 85%  $\text{TiO}_2$ . This is mixed with high-purity coke and chlorinated at 850–950°C in a fluidised bed reactor to produce titanium tetrachloride ( $\text{TiCl}_4$  or “tickle”). This is oxidised in air at elevated temperatures to produce  $\text{TiO}_2$ , which is then calcined to remove residual chlorine and hydrochloric acid. The absence of an effluent and a consequent disposal problem has helped make the chloride process the preferred route in modern plants despite the disadvantage of a complex process and the necessity for a high- $\text{TiO}_2$  feedstock.

Rutile production capacity is limited, and therefore the shortfall in natural high- $\text{TiO}_2$  feedstock is made up by upgrading ilmenite. One method is the conversion of ilmenite containing 42–58%  $\text{TiO}_2$  to a “beneficiated ilmenite” or “synthetic rutile” containing 91–96%  $\text{TiO}_2$  by reduction of the iron in ilmenite to the metallic state using sub-bituminous coal both as a source of fuel and as a reductant. Another method is the production of a titaniferous slag, which involves smelting a mixture of ilmenite concentrate and coal in a large rectangular electrical furnace equipped with graphite electrodes.

Titanium metal is obtained in the pure form by the Kroll process. The oxide is treated with chlorine to form titanium tetrachloride, a volatile liquid, and the liquid is reduced with magnesium in a closed iron chamber to yield metallic titanium. The metal is then melted and cast into ingots.

## ERMS and EARS

Austpac Gold NL has developed a specialised proprietary process, termed Enriched Roasting Magnetic Separation (ERMS; Austpac, 1997), for producing synthetic rutile from ilmenite sands at Westport, and are now seeking to also apply the process in other parts of the world. In the ERMS process, a heavy mineral concentrate is roasted in a controlled atmosphere to selectively induce very high magnetic susceptibility in any contained ilmenite. This is followed by magnetic separation of the ilmenite. The ilmenite is leached with hydrochloric acid to remove iron and produce synthetic rutile with 96–97%  $\text{TiO}_2$ . Further processing reduces the iron content to less than 0.1% and results in “Supergrade” pigment with more than 99%  $\text{TiO}_2$ . Another Austpac Gold process, the Enhanced Acid Regeneration System (EARS), regenerates hydrochloric acid from the iron chloride produced during synthetic

rutile manufacture. The solution is evaporated to produce iron chloride pellets which are fed into a pyrohydrolysis reactor, producing hydrochloric acid, magnetite, steam and carbon dioxide.

## New Zealand Occurrence and Resources

The occurrence of titanium in New Zealand has been reviewed by Williams (1974), Officers of the New Zealand Geological Survey (1981), and Brathwaite and Pirajno (1993), and Railton and Watters (1990) listed the occurrences of titanium minerals. The most significant occurrences are ilmenite in beach sand placers on the West Coast, South Island (Fig. 1). Ilmenite also occurs in beach sands at several locations along the eastern coast of Coromandel Peninsula, and associated with titanomagnetite beach sands between Muriwai and Manukau Heads. Magmatic segregation deposits of ilmenite are present in Northwest Nelson, Marlborough and central Fiordland. Minor concentrations of rutile have been recorded in several beach sand deposits in Fiordland and at Orepuke in western Southland.

### Magmatic deposits

Ilmenite occurs as stratiform segregations with magnetite in diorite at Mt Pisgah in Northwest Nelson, in gabbroic rocks on Mt Tapuaenuku and Blue Mountain in the Kaikoura Ranges, and in gabbro at Mt George in Fiordland.

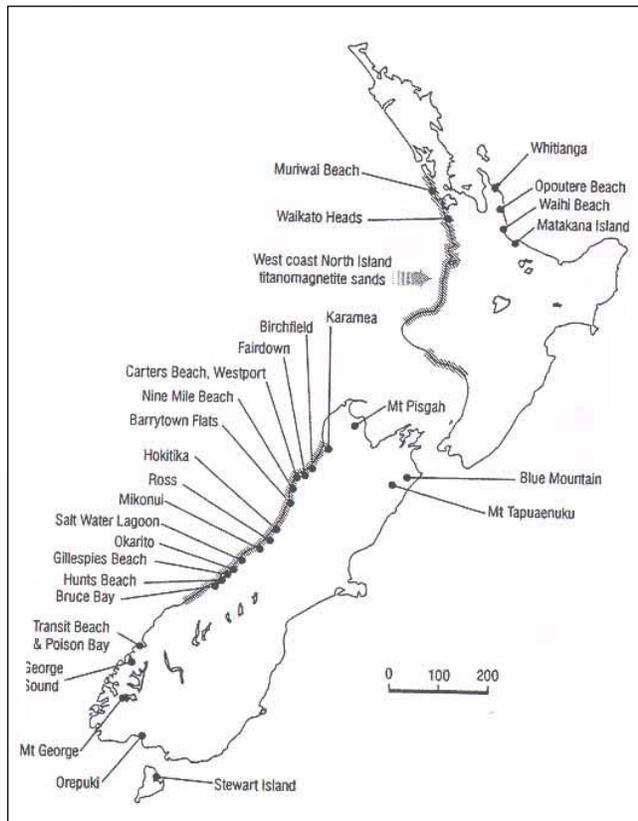


Figure 1: Location of titanium deposits in New Zealand.

**Mt Pisgah, Northwest Nelson:** Disseminated ilmenite and magnetite occur in narrow bands in diorite near the summit of Mt Pisgah, near Canaan (Williams *et al.*, 1959). The magnetite contains exsolved ilmenite.

**Mt Tapuaenuku, Kaikoura:** Pockets of ilmenite-magnetite are present in layered gabbroic rocks within the main body of the Tapuaenuku Complex (Pirajno, 1980; Baker *et al.*, 1994). The Early Cretaceous complex is 6.5 km long and 4 km wide and intrudes Torlesse Supergroup rocks. The ilmenite and magnetite occur as interstitial blebs in a silicate matrix and are accompanied by minor quantities of pyrite, chalcopyrite and pyrrhotite. Concentrations of these opaque minerals may locally reach 70% by volume.

**Blue Mountain, Kaikoura:** Ilmenite with some titaniferous magnetite occurs as disseminations in gabbro dikes and layered olivine gabbros in the Blue Mountain Igneous Complex. The complex is a central-type alkali ultrabasic-gabbro ring complex of Early Cretaceous age (Grapes, 1975), which intrudes Torlesse Supergroup rocks 15 km west of Ward, Marlborough. It is 1.5 km x 1 km in area, with steep dips around the margin and more gentle dips near the centre.

**Central Fiordland:** Stratiform bands of massive ilmenite and magnetite are present in a northerly trending discontinuous band of gabbroic to dioritic intrusions that extends over a distance of about 90 km, from Mt Soaker south to Lake Poteriteri (Oliver and Coggon, 1979; Pirajno, 1980; Gibson, 1982). The intrusions are lenses and tabular bodies representing remnants of sills deformed during metamorphism and folding. Gabbroic phases attain a thickness of over 200 m and in places contain magmatic segregations of magnetite and ilmenite. The magnetite-ilmenite rich layers contain from 3 to 25% magnetite, slightly lesser ilmenite, and up to 2% sulphide (pyrite, pyrrhotite and minor chalcopyrite). The magnetite concentrates contain 1.2 to 1.4%  $V_2O_5$ . Mt George is the best known example, although several others have been described including Howitt Peaks (Wood, 1973a), Mt Troup near Doubtful Sound (Hancock in Williams, 1974, p 395), Wilmot Pass (Wodzicki in Williams, 1974, p 397), Lake Roe and Bow Lake in the Lake Hauroko area (Hancock in Williams, 1974, p 397-8), and the Northwest Arm of Lake Te Anau (Wood, 1973b).

Mineralisation was discovered at Mt George by K.C. Walshe in the 1960's and explored by Consolidated Silver between 1970 and 1972 (Codling, 1972; Main, 1972). The host intrusion is Early Cretaceous in age (see Brathwaite and Pirajno, 1993, p 22) and was described by Gibson (1982) as a sequence of anorthositic metagabbro overlying hornblende metagabbro, with amphibolite and hornblende pegmatite at the base. The magnetite-ilmenite segregations are bands varying from 2 to 50 cm thick with the iron oxides usually concentrated at the base. They generally contain about 20% magnetite and 16% ilmenite. Magnetite concentrates contain an average of 1.2%  $V_2O_5$ .

### Shoreline placer ilmenite

**West Coast, North Island:** Ilmenite is present in ironsand deposits north of Waikato Heads on the west coast of the North Island (Nicholson and Fyfe, 1958; Hamill and Ballance,

1985). The highest contents recorded in reconnaissance sampling by Nicholson and Fyfe (1958) were from the southern end of Muriwai Beach (Q11/37408510) 11.0%, middle Piha dunes (Q11/41207170) 12.1%, and Pararaha dunes (north of Whatipu, Q11/42706410) 16.0%. However, channel samples taken from the tidal zone of the beaches by Hamill and Ballance (1985) contained up to only 10% ilmenite with many samples lacking ilmenite altogether. The ilmenite of this region has a relatively low TiO<sub>2</sub> content (35–42.5%). The main ilmenite source is considered to be the rhyolitic volcanic rocks of the Taupo Volcanic Zone, washed down the Waikato River and deposited by long shore drift.

**Coromandel Peninsula:** Ilmenite occurs in significant concentrations in some Holocene beach and dune sands on the east coast of the Coromandel Peninsula and on Matakana Island. McLaughlin and others (McLaughlin, 1971, 1973, 1975, 1978) explored onshore and offshore deposits at Whitianga (Wharekaho Bay) and Wharekawa (Opoutere Beach), drilling more than 1000 m in holes generally less than 15 m deep. At Whitianga, concentrations averaging more than 50% heavy minerals occur in beach, dune, estuary

and bay sediments. The heavy mineral fraction contains about 75–80% ilmenite along with lesser hematite, titanomagnetite, hypersthene and zircon. Estimated resources are 1.125 Mt of concentrate containing 40% TiO<sub>2</sub>, the ilmenite assaying 42.6% TiO<sub>2</sub>. At Opoutere Beach, concentrations averaging more than 50% heavy minerals occur in dune deposits behind the present beach. The heavy mineral fraction contains 60–80% ilmenite along with lesser titanomagnetite, hypersthene, hematite and zircon. Estimated resources are 2.5 Mt of concentrate grading about 40% TiO<sub>2</sub>, the ilmenite assaying 45.6% TiO<sub>2</sub>.

A survey of the ilmenite beach and dune sands at Waihi Beach included nine posthole bores with an average depth of 4 m (Nicholson *et al.*, 1958; Kear and Waterhouse, 1961, p. 443). These contained an average of 5.9% ilmenite. Three magnetically separated samples contained 40.0%, 34.4%, and 27.2% TiO<sub>2</sub> respectively.

The barrier dune sands of Matakana Island were drilled by New Zealand Forest Products Limited who estimated blacksand volumes of 197 Mm<sup>3</sup> at 1.5% ilmenite in the upper foredune section, and 545 Mm<sup>3</sup> at 0.36% ilmenite in the lower

Grid Ref.	Location	Ilmenite (Mt)	Grade (% ilmenite)	Other recoverable minerals	Reference
L27/345978	Karamea North	2.5	6%	zircon, monazite	Zuckerman (1972b)
L27/332859	Karamea South	0.65	3.6%	zircon, monazite	Zukerman (1972b)
K29/085474	Birchfield	1.0	5.8%	zircon, monazite	Zuckerman (1972a)
K29/008402	Fairdown	no estimate			Buller Minerals (1971a, 1972b)
K29/889388	Carters Beach	6.5-9.6	7.6-15%	zircon, monazite, gold	McPherson (1978)
K29/819333	Nine Mile Beach North	1.8-2.4	5.4-7.4%	zircon, monazite, gold	McPherson (1978)
K29/820269	Nine Mile Beach South	0.45-0.58	10-13%	zircon, monazite, gold	McPherson (1978)
K31/709876	Barrytown Flats	6.9	13.8%	zircon, monazite, gold	Western Ilmenite (1991)
J32/571497	New River	no estimate			Howe (1975)
J32/527411	Hokitika North (Awatuna)	0.42	6.0%	zircon, monazite, gold	Painter (1972c)
J33/392269	Hokitika	0.65	5.9%	zircon, monazite, gold	Painter (1973a)
J33/357179	Hokitika South	3.0	6.4%	zircon, monazite, gold	Painter (1972d)
I33/288105	Ross	0.56	5.5%	zircon, monazite, gold	Painter (1973b)
I33/256077	Mikonui	0.17	5.2%	zircon, monazite, gold	Painter (1972e)
I34/155999	Ounatai	small			Caffyn (1971a)
I34/960888	Saltwater Lagoon	0.51	10.1%	zircon, monazite, gold	Caffyn (1971e), Painter (1972a)
H35/736663	Five Mile Beach, Okarito	0.47	5.6%	zircon, monazite, gold	Caffyn (1971g), Painter (1972a)
H35/679598	Omoeroa	no estimate	1.6%		Caffyn (1971b)
H35/528501	Gillespies Beach	0.44	3.2%	gold	Caffyn (1971d), Painter (1972f)
G36/417344	Hunts Beach	0.31	11.0%	zircon, monazite	Caffyn (1971f), Painter (1972f)
G36/376297	Bruce Bay	0.12	6.0%	zircon, monazite	Caffyn (1971c), Painter (1972f)

Table 2: Ilmenite resources, West Coast, South Island (modified after Officers of New Zealand Geological Survey, 1981).

20 m silty section (Hancock & Associates, 1979, 1981). Indicated grades of gold and silver were 2.6 and 2.2 mg/m<sup>3</sup> respectively, with zircon concentrations of 0.23% or less.

**West Coast, South Island:** Ilmenite is present in coastal sand deposits along 320 km of coastline between Karamea River in the north and Bruce Bay in the south. The deposits consist of narrow, elongate Holocene beach and dune deposits, generally parallel to and backing the modern storm beach (e.g. Barrytown, Suggate, 1989). In some areas, ilmenite occurs in a succession of raised (interglacial) beach deposits which may be cemented to varying degrees. In the beach sands, ilmenite has been concentrated by wave action into blacksand leads with average grades of 10–25% ilmenite. In the dune sands, ilmenite occurs in concentrations generally less than 6%. Other associated heavy minerals include garnet, magnetite, zircon, and rutile, and traces of gold, monazite, cassiterite, beryl, uranothorite, scheelite, cassiterite, and xenotime (Hutton, 1950; McPherson, 1978; Minehan, 1989). The ilmenite has abundant silicate inclusions and consequent low titanium content (45–47% TiO<sub>2</sub>). The ilmenite was derived mainly from garnet schist of the Haast Schist along the Southern Alps (Gill in McPherson, 1978).

Reconnaissance exploration has been carried out over several periods by the Department of Scientific and Industrial Research (Nicholson *et al.*, 1958; Marshall *et al.*, 1958; McPherson, 1978), and by private companies, including Lime & Marble in joint venture with Rutile & Zircon Mines Ltd (Pullar and Henderson, 1966; Pullar and Pullen, 1967a, 1967b, 1968), Buller Minerals (Buller Minerals, 1971a, 1971b, 1972a, 1972b), and Carpentaria Exploration (Caffyn, 1971a–g, 1976; Carpentaria Exploration, 1970a, 1970b, 1973; Best, 1972; Zuckerman, 1972a, 1972b; Painter, 1972a–f, 1973a, 1973b; Beck, 1976). These surveys indicate that the largest deposits are Karamea North, Birchfield, Fairdown, Carters Beach, Nine Mile Beach, Barrytown and Hokitika South, individually with reserves in the range of 1 to 10 Mt of contained ilmenite at average grades of 6 to 13.8% ilmenite (Table 2).

At Westport, McPherson (1978 - Tables 16 and 17, Fig. 54) estimated a mineable resource in the range of 17 to 31.5 Mt. Subsequently, Austpac Gold and others have explored the ilmenite deposits near Westport and estimated a resource of 122 Mt of sand with an average grade of 4.5% ilmenite, equivalent to 5.5 Mt of contained ilmenite (M. Turbott, written comm., 1997). Austpac has developed proprietary ERMS and EARS processes for separation of the ilmenite from garnet and other heavy minerals, and manufacture of high purity synthetic rutile, which they consider could result in development of the Westport deposits. They are currently preparing a feasibility project for a 10,000 t/year “Supergrade” titanium dioxide plant.

Exploration of the Barrytown deposit initially by Carpentaria Exploration Co. Pty Limited, followed by Grampian Mining Co. Limited (wholly owned subsidiary company of Fletcher Challenge Limited; Mann and James, 1989), and

subsequently by Westland Ilmenite Limited (North Limited), has indicated the presence of 50 Mt of potentially mineable sand at an average grade of 13.8% ilmenite (6.9 Mt), 0.2% zircon, 100 mg/m<sup>3</sup> gold, and less than 0.1% each of monazite and rutile (Westland Ilmenite, 1991). Westland Ilmenite Limited in joint venture with Otter Gold Mines lodged an application for a mining permit in September 1995, with a proposal to mine 3 Mt of sand per year to produce 250,000 t of ilmenite concentrate annually.

**Southland:** Ilmenite, along with magnetite and in places zircon, is found in several Holocene beach placer deposits including Coal River (Hancock, 1972), Grace Burn (Watters, 1980), Te Wae Wae Bay (Nicholson, 1969), Orepuki and Riverton (Martin and Long, 1960; Nicholson, 1969; Wood, 1969). At Te Wae Wae Bay, Nicholson (1969) reported 3.46% ilmenite in a 2.5 m augered sample (his No. 39A). At Orepuki, the heavy mineral sand contains 3–17% ilmenite and 0.1–1.1% zircon, and the ilmenite concentrate assayed 26% TiO<sub>2</sub> (Martin and Long, 1960).

**Stewart Island:** Small quantities of high purity black sand are present on several beaches on the northeast coast of Stewart Island (Williams and Mackie, 1959). A sample from Ringa Ringa beach contained 85% magnetite, and 13% ilmenite assaying 43.5–44.0% TiO<sub>2</sub>.

### Shoreline placer rutile

Rutile occurs widely as a minor or trace component in beach placers in the South Island, along with garnet and in some locations, zircon and kyanite. The West Coast ilmenite beach sands contain traces of rutile, usually in the range of 0.02–0.11%. McPherson (1978, p. 78) reported 2.2% TiO<sub>2</sub> in the non-magnetic heavy mineral fraction of one sample from the western end of Carters Beach, Westport. Heavy mineral beach sands at Transit Beach and Poison Bay, near Milford Sound contain up to 1% rutile and zircon, with abundant garnet and hornblende (Williams, 1974; Watters, 1977; Layton and Associates, 1982). Ryan (1982) estimated an inferred resource of 1.5 Mt of sand in the sand dunes of Poison Bay. Morgan (1927) quoted earlier references to rutile in Wet Jacket Arm, Dusky Sound, in “sand with 66% TiO<sub>2</sub>”. Rutile is present in black sand at Orepuki, Southland and one sample was reported to contain 0.16% rutile (Williams, 1974, p. 141).

### Alluvial placer rutile

Hutton (1950) reported that rutile was present in most of the finer fractions of gold dredge concentrates from alluvial gravels in the West Coast region. In Northwest Nelson, detrital rutile has been reported in Atkin’s Creek and an adjacent stream in the Canaan valley area (Williams *et al.*, 1959), and in the Anatoki River (Williams, 1974).

### Shoreline placer titanomagnetite

A very large resource (500 Mt) of heavy mineral beach sand along the west coast of the North Island contains titanomagnetite (averaging 23% of the raw sand) with a TiO<sub>2</sub> content of 7–8%. Ilmenite is also locally present (see above).

## Past Production, Resources and Future Potential

There has been no production of titanium oxide from New Zealand deposits, although potentially large resources have been identified, particularly in the Westland ilmenite beach sand deposits (Table 2). Ilmenite makes up 5–14% of the sands, but the titanium oxide content of the ilmenite is low (45–47% TiO<sub>2</sub>) by world standards due to inclusions of garnet and other silicate minerals. This factor has so far precluded mining of the Westland deposits, but proprietary processes have been developed to upgrade the ilmenite to a high TiO<sub>2</sub> product. The largest ilmenite deposits are at Barrytown (6.9 Mt of ilmenite) and near Westport (5.5 Mt of ilmenite) and these are likely to be the first deposits to be exploited in any future mining.

The very large resources of titanomagnetite in the west coast North Island ironsands contain 7–8% TiO<sub>2</sub>, but the recovery of titanium from the titanium-bearing slag produced by New Zealand Steel, as a result of smelting of the Waikato North Head titanomagnetite ironsand, is not economic with currently available technology. However the slag is exported and used overseas in steel production.

## Future Trends

Demand for titanium is expected to increase because of the superior qualities of titanium dioxide as a white pigment and of titanium metal in situations requiring high strength and resistance to heat. Nevertheless, there is potential substitution of titanium alloys used in aerospace applications by lithium-aluminium alloys or carbon-epoxy composites.

Increasing environmental controls will result in wider use of the chloride process in titanium dioxide production because of the lower quantities of waste byproducts, compared with the sulphate process. This will require increasing amounts of high grade TiO<sub>2</sub> feedstock in the form of synthetic rutile or slag. There is also strong pressure to reduce the radioactive content of feedstocks (chiefly monazite and thorite), which reduces the marketability of some beach sand ilmenite.

New developments in process technology are required to utilise the anatase deposits in Brazil and perovskite deposits in the USA.

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