

Mineral Commodity Report 19 - Beryllium, Gallium, Lithium, Magnesium, Uranium and Zirconium

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Beryllium

Discovery and origin of names

Precious stone varieties of the beryllium mineral beryl have been known for six thousand years. When polished, beryl served as an eyeglass, for example, it was used by Nero whilst observing Rome on fire in 64 A.D.. Beryllium was discovered as an oxide, now known as beryllia, in beryl and in emeralds in 1798 by the French chemist Louis Vauquelin. The pure metal was isolated in 1828 independently by Friedrich Wöhler in Germany and Antonine Bussy in France.

Beryllium was first called glucinum from the Greek *glykys*, for sweet, because the soluble compounds are sweet-tasting. However, Wöhler established the name beryllium, after the chief mineral beryl, named from the Greek *beryllos*.

Major ores and minerals

Beryllium does not occur free in nature, but is an essential constituent in about 40 minerals and may also be present in some 50 others, including plagioclase, micas and clays. This widespread occurrence results from its ability to replace silicon in minerals. Beryl and bertrandite are the principal ore minerals (Table 1), although deposits of chrysoberyl and phenakite may become economically significant in the future. Rare gem forms of beryl include green emerald, blue aquamarine, pink morganite and colourless goshenite.

Properties

Beryllium is one of the alkaline-earth metals of Group IIa of the periodic table. It is a steel grey coloured metallic element, one of the lightest of all metals, and has one of the highest melting points of the light metals. It has excellent

thermal conductivity, is nonmagnetic and has a high permeability to X-rays. Its modulus of elasticity is about one third greater than that of steel and, although brittle, it has a high strength per unit weight. It resists attack by concentrated nitric acid, and tarnishes only slightly in air, becoming covered with a thin layer of oxide.

The properties of some beryllium minerals are listed in Table 1. The main beryllium mineral, beryl, occurs as hexagonal crystals that may grow to a large size, up to 0.5-0.9 m across and several metres long. The largest beryl crystal yet discovered, from the Picuí deposit in Paraíba, Brazil, weighed 200 t. Emerald is a transparent, intensely green variety of beryl.

Formation

Beryl is found in coarsely crystalline pegmatite dikes that occur peripheral to some granitic intrusions and represent the late stage crystallisation of residual fluids. The pegmatites are composed of quartz, sodic plagioclase and microcline with or without spodumene, muscovite or lepidolite. Such pegmatites are common in the ancient continental shield areas of Canada, Australia and Africa; in the USA, they are found in the southern Appalachians, New England and the Black Hills of South Dakota.

Beryllium is also found in replacement deposits including epithermal mantos in tuffs, tactite or emerald-bearing schists. An important example is Spor Mountain, Utah, USA, where bertrandite mineralisation is associated with epithermal alteration of rhyolitic, water-laid tuffs of Pliocene age, particularly in parts of the tuff containing carbonate pebbles eroded from Paleozoic limestone and dolomite. The main alteration products are smectite, quartz, fluorite and adularia. Grades are typically less than 0.5% Be. The chrysoberyl deposits of the Seward Peninsula, Alaska, are replacement bodies in limestone and consist of very fine grained fluorite, diaspore and chrysoberyl.

Symbol	Be	Ga	Li	Mg	U	Zr
Atomic no.	4	31	3	12	92	40
Atomic wt	9.01	69.72	6.94	24.31	238.03	91.22
Specific gravity	1.85	5.90	0.53	1.74	19	6.51
Valence	2	2,3	1	2	2,3,4,5,6	2,3,4
Melting point °C	1287	29.76	180	650	1132	1855
Boiling point °C	2471	2204	1342	1090	3818	4409
Crustal abundance	2-3.5 ppm	0.0015%		2%	2 ppm	
Preferred analysis method	Atomic absorption spectroscopy	Atomic absorption spectroscopy	Atomic absorption spectroscopy	XRF	XRF	XRF
Routine detection limit	0.1 ppm	1 ppm	1 ppm	100 ppm	0.2 ppm	1 ppm

Name, Formula	Colour	Hardness	Specific gravity	Lustre	Crystal form	Transparency	Fracture
Barylite BaBe ₂ Si ₂ O ₇	colourless, white, yellow	7	4	silky, greasy or vitreous	orthorhombic or monoclinic	transparent- translucent	brittle
Bertrandite Be ₄ Si ₂ O ₇ (OH) ₂	colourless, white, pale yellow	6-7	2.6	vitreous to pearly	orthorhombic	transparent	brittle
Beryl Be ₃ Al ₂ Si ₆ O ₁₈	white, pale- blue, green	7.5-8	2.6-2.9	vitreous	trigonal	transparent- translucent	uneven to conchoidal, brittle
Chrysoberyl BeAl ₂ O ₄	green, yellow, red	8.5	3.5-3.8	vitreous	orthorhombic	transparent- translucent	conchoidal to uneven, brittle
Eudidymite NaBeSi ₃ O ₇ (OH)	colourless, white, yellow, blue	6-7	2.55	vitreous	monoclinic	transparent- translucent	brittle
Helvite (Mn,Fe,Zn) ₄ Be ₃ Si ₃ O ₁₂ S	brown, yellow, grey	5.5-6.5	3.2-3.4	vitreous to resinous	cubic	transparent- translucent	conchoidal to uneven, brittle
Phenakite/ Phenacite Be ₂ SiO ₄	colourless, white	7.5-8	2.9-3.0	vitreous	trigonal	transparent	conchoidal, brittle

Table 1: Properties of some beryllium minerals.

Beryllium is recovered from hydrothermal-pneumatolytic skarn and greisens that also contain tin, fluorite and/or tungsten. Skarns may contain up to 0.7% BeO in the mineral helvite. Beryl and bertrandite are also found associated with fluorite in mica quartz greisen near a granitic intrusion in Park County, Colorado. Phenakite and bertrandite occur with scheelite, fluorite and pyrite in White Pine County, Nevada. Other beryllium deposits are in Sea Lake, Labrador, Canada, as barylite; and in Coahuila, Mexico as bertrandite.

Nepheline syenite and other nepheline-bearing rocks may contain up to 0.1% BeO, and at the rare metals deposit at Thor Lake, near Yellowknife in the Northwest Territories of Canada, five deposits have been identified as a large resource of tantalum-niobium, rare earths, zirconium, gallium and beryllium. They are contained within a large gabbroic to syenitic and granitic body of alkaline affinity with resources of 1.6 Mt grading 0.85% BeO (see rare earths mineral commodity report; Christie and Brathwaite, 1998a).

Beryllium has been recognised as concentrating in coals, with an average of 46 ppm in coal ash.

Uses

Beryllium is mostly used in the production of special alloys (75%), and to a lesser extent as beryllium oxide (15%), and beryllium metal (10%).

Beryllium is added to alloys to increase heat resistance, corrosion resistance, hardness, insulating properties and better casting qualities. Beryllium-copper alloys, containing about 2% Be, are the most important, although beryllium-aluminium alloys, with about 65% Be and 31% Al, are becoming increasingly used in aerospace, electronics, telecommunications, consumer products and robotics. Beryllium-copper alloys are manufactured into springs, connectors, and switches for use in applications in automotive, aerospace, radar and telecommunications industries, and in factory automation, computers, home

appliances, and instrumentation and control systems. A rapidly expanding use is in oil and gas drilling equipment. Beryllium alloys are also used in precision moulds for the plastics industry, and in consumer leisure markets they are used in high quality golf club heads, as well as in consumer electronics such as stereo systems, VCRs, portable telephones, miniature radios and video cameras.

Beryllium oxide (beryllia) is used in the manufacture of high temperature ceramics and high-quality electrical porcelains, in microwave tube parts (e.g. cathode supports, envelopes, spacers, helix supports, collector isolators, heat sinks and windows), in solid state electronic devices, in bores or plasma envelopes for gas lasers, and as a slurry for coating of graphite crucibles.

Beryllium metal is used in nuclear reactors as a moderator to lessen the speed of fission neutrons and as a reflector to reduce leakage of neutrons from the reactor core.

Because beryllium is relatively transparent to X-rays it is used in ultra thin sheet or foil form as window material in x-ray tubes for transmission of rays and to filter out electrons.

Price

Prices for beryl (10% BeO) in August 1999 were US\$75-80/short ton BeO cif (Mining Journal, August 20, 1999).

World production and consumption

Total world production of beryllium in 1998 was estimated at 330 t of contained beryllium. Beryl was mined at operations in China (55 t of contained Be in 1998), Russia (40 t), Kazakhstan (4 t) and Brazil. Sporadic output is occasionally recorded in Zimbabwe, Zambia, Madagascar, Argentina and Portugal. Bertrandite is produced from Spor Mountain area of Utah, with an output of about 230 t of contained beryllium in 1998.

World resources of contained beryllium have been estimated by the US Bureau of Mines to exceed 1.3 Mt, with 35% in

Brazil, 16% in India, 15% in the Commonwealth of Independent States (CIS), and 7-8% each in the USA and Argentina. In China, the largest resources are found in Inner Mongolia.

Ore processing, smelting and refining

Two processes are used to extract beryllium oxide or hydroxide from beryl ore. In the first the beryllium is selectively extracted by roasting beryl with sodium fluorosilicate at 700-750°C and leaching the product with water to extract soluble beryllium fluorides (Copaux process). Beryllium is recovered from the fluoride leach liquors by precipitation as the hydroxide at pH 12. In the second method, the fuse-quench process, beryl is melted in an electric furnace at 1600-1650°C and quenched to a glass by pouring into water. The glass is devitrified by heating to 900-950°C to make it more reactive with dilute acid. The devitrified glass is broken down by heating with sulphuric acid.

Bertrandite and berylite ores are less refractory than beryl and can generally be treated with moderately strong acid to extract the beryllium directly. At Spor Mountain the bertrandite ore is wet-milled and the slurry is leached with sulphuric acid at temperatures near the boiling point. A leach liquor containing BeSO_4 separated from the solids is concentrated using solvent extraction. The next stage forms beryllium carbonate, $2\text{BeCO}_3 \cdot \text{Be}(\text{OH})_2$, which precipitates out on heating. Further heating forms $\text{Be}(\text{OH})_2$. After filtering, this product is shipped to the company's Elmore, Ohio, plant for processing into metal, beryllium-copper alloy or beryllia ceramic products.

New Zealand occurrence and resources

Beryl occurs in pegmatites near Charleston on the West Coast, and on the north shore of Paterson Inlet, Stewart Island (Fig. 1). The pegmatites near Charleston are hosted in banded granitic Constant Gneiss and contain coarse grained quartz, feldspar, muscovite and biotite. Beryl occurs as columnar, pale green to colourless crystals up to 125 mm across and containing 12.82% BeO (Hutton and Seelye, 1945; Officers of New Zealand Geological Survey, 1970a). At Paterson Inlet, beryl occurs as fine grained crystals in association with abundant tourmaline (McKay, 1890). Hutton and Seelye (1945) referred to the existence of beryl at Dusky Sound, but gave no specific location or reference.

In the Canaan Valley, Pikiiruna range, quartz veins associated with Separation Point Granite contain rare, blue and colourless beryl crystals, and scheelite (Williams et al., 1959). The beryl is mostly very fine grained, but a few crystals up to 8 mm in size are present. Beryl is also present in nearby stream alluvium (Officers of New Zealand Geological Survey, 1970a).

Analyses from the ilmenite-bearing beach sand on the West Coast, during prospecting in the 1970s, showed traces of beryl. In the Birchfield licence, it comprised 0.01% of the heavy mineral fraction, and 0.02% at Hokitika (Zuckerman, 1972; Painter, 1973). Hutton (1950) noted that some West Coast dredge concentrates contained rare grains of gadolinite that were probably eroded from pegmatites in the Karamea granite.

Cohen et al. (1967) noted high background concentrations of beryllium in the Hawks Crag Breccia of the lower Buller Gorge area (see uranium section).

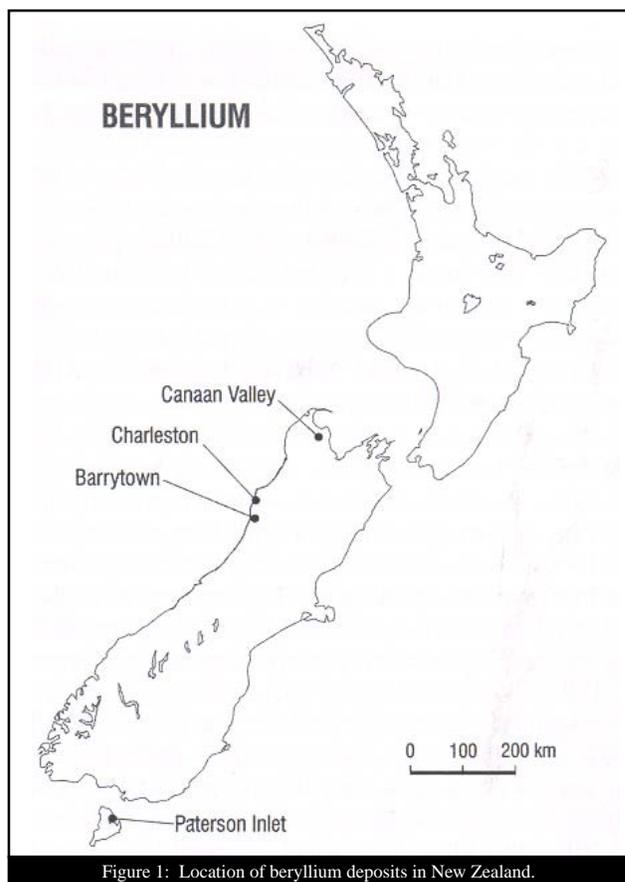


Figure 1: Location of beryllium deposits in New Zealand.

Future trends

Defense industry applications of beryllium have declined, whereas there is an increasing use of beryllium alloys and ceramics in the telecommunications and electronics industries, and of beryllium-copper alloys in the automotive industry. The increased use of beryllium-aluminium alloys compared with beryllium-copper alloys is expected to increase the demand of beryllium because of the higher content of beryllium in beryllium-aluminium alloys.

Gallium

Discovery and origin of names

Gallium was discovered in 1875 by Paul-Émile de Boisbaudran, who observed its principal spectral lines while examining material separated from sphalerite. A year later he isolated the element in its metallic state by electrolysis of a solution of the hydroxide in KOH. He found that its properties coincided with those Dimitry Mendeleev had predicted a few years earlier for eka-aluminium, the then undiscovered element lying between aluminium and indium in his periodic table. Boisbaudran named the new element in honour of his homeland Gaul, derived from the Latin *Gallia*, France, and also from the Latin, *gallus*, a translation of Lecoq, a cock.

Major ores and minerals

Gallium does not occur free in nature or as a major constituent of any minerals, apart from gallite (CuGaS_2), but it is present in trace quantities in most aluminosilicate minerals, particularly bauxite, some clays (e.g. kaolin and diaspore), sphalerite, pyrite and magnetite, as well as in coal.

Properties

Gallium is a metallic element in Group IIIa of the periodic table, and is one of the few metals that is liquid at or near room temperature. Further, it remains in the liquid state over a wider range of temperatures than any other element (30°C to 2403°C). It is blue-grey in colour as a solid and silvery as a liquid. The solid metal is soft and exhibits a conchoidal fracture similar to glass. Gallium wets glass or porcelain, and forms a brilliant mirror when it is painted on glass. Somewhat similar to aluminium chemically, gallium slowly oxidises in moist air until a protective film forms, and it is attacked only slowly by acids. Gallium readily alloys with most metals.

Formation

There are no concentrated deposits of gallium, instead gallium is produced as a byproduct of aluminium production from bauxite, and less commonly from zinc production from sphalerite. The occurrences of bauxite and sphalerite ores are described in the aluminium and lead-zinc mineral commodity reports respectively (Christie et al., 1993; Christie and Brathwaite, 1995a). Gallium is more abundant in bauxites derived from granitic and alkalic rocks, and the Ga:Al ratio increases with weathering intensity. In zinc ores, the gallium contents are higher in replacement deposits formed at lower temperatures. The Tri-State and Upper Mississippi Valley districts have been the main source of US production.

The Tsumeb deposit in Namibia, a pipe-like replacement body of copper-lead-zinc sulphides, is unique in its production of a germanite-renierite concentrate, which has been the dominant source for European refining of gallium and germanium. The deposit has been the source for most of the other reported gallium minerals from oxidised ores.

Uses

Approximately 95% of gallium consumed is used in the electronics industry, mainly in semiconductors for transistors, rectifiers, light sources, lasers and photocells. Minor quantities have been used in thermometers, low-melting solders, as a heat-transfer fluid, in arc lamps, batteries, vanadium-gallium superconductors, and in catalyst mixtures.

Ore processing, smelting and refining

Bauxite ore is dissolved in sodium hydroxide solution, producing a gallium-bearing sodium aluminate solution, with recovery accomplished by fractional carbonation and electrolysis.

Gallium is also recovered in smelting sphalerite. Gallium is reduced with the zinc metal, which is distilled off. The gallium is recovered from the flue dust and from the residues of the zinc purification process. The material is dissolved in aqueous hydrochloric acid and then gallium is separated by solvent extraction. The gallium is recovered from the organic solvent, further purified, and then reduced to the metal.

New Zealand occurrence

Gallium is present in muds and sinters of geothermal fields of the Taupo Volcanic Zone. Crump (1994) reported gallium concentrations ranging between 8 and 144 ppm in 48 surface samples from 11 major geothermal fields (Fig. 2). Crump considered that in the mud samples, the gallium

was probably present in kaolinite, substituting for aluminium. He noted that mud samples from Champagne Pool (Waiotapu), Lagoon Corner (Rotokawa) and Lake Rotoa-Tamaheke (Rotorua), that have high gallium concentrations (>70 ppm), also contain high concentrations of antimony (400->5000 ppm) and arsenic (800->10,000 ppm). These two elements form colloids that are efficient scavengers of metals. Co-precipitation of gallium with these colloids is a possible deposition mechanism.

Future trends

Gallium could be recovered from coal ash and coal, and extracted from polymetallic ores by leaching. Demand may increase for use in gallium-based electronic devices, in equipment converting solar energy to electricity, and, possibly, in commercial microwave applications.

Lithium

Discovery and origin of names

The lithium-containing minerals, petalite and spodumene, were discovered by Jose de Andrada between 1790 and 1800 in Sweden. Lithium was discovered in 1817 by Johann Arfvedson in Sweden during an analysis of petalite ore. Humphry Davy and Brandé independently isolated the metal in 1818 by electrolysis of lithium oxide. The name lithium is from the Greek *lithos* "stone", because it was first discovered in a mineral.

Major ores and minerals

Lithium is not found free in nature, but it occurs in small amounts in nearly all igneous rocks and in the waters of many mineral springs. Spodumene, lepidolite, petalite and



Figure 2: Location of lithium and gallium deposits in New Zealand.

amblygonite (Table 2) are the most common of the 40 or so lithium minerals.

Properties

Lithium is the first element in Group Ia of the periodic table, the alkali metals. It is white, with a silver lustre, and has a hardness of 0.6 (softer than lead). It is the lightest solid element, with a density only about half that of water. It is highly reactive and resembles sodium in its chemical behaviour. It reacts with water (but not as vigorously as sodium), the non-metals, inert gases excepted, most of the metalloids, and many of the metals. It tarnishes instantaneously and corrodes rapidly upon exposure to air; when it is stored it must be immersed in a liquid such as naphtha. Lithium imparts a crimson colour to a flame, but when the metal burns strongly the flame is a dazzling white.

The properties of some lithium minerals are listed in Table 2.

Formation

Lithium is recovered from brines and from minerals in granite pegmatites, and in the future may also be recovered from clays.

Lithium-bearing granite pegmatites are found as dikes peripheral to granite intrusions, and were formed by crystallisation of late stage residual fluids. Lithium occurs in a paragenetic range from early-stage minerals like iron-rich spodumene through intermediate stages (spodumene, petalite, lepidolite and amblygonite) to low temperature hydrothermal alteration products such as eucryptite, bikitaite and cookeite. Examples occur in King Mountain, North Carolina; Black Hills of South Dakota; Bernic Lake, Manitoba (Tanco pegmatite); Aracuai, Minas Gerais, Brazil; Altai Mountains, China; Chita region, Russia; Bikita mine in Zimbabwe (Bikita pegmatite); Karibib, Namibia (Rubicon and Helicon pegmatites); "tin mineral province" in Zaire; and Greenbushes pegmatite field, Western Australia.

Lithium-rich brines are found in areas of volcanic activity such as Imperial Valley, California. Reykjanes Field, Iceland,

and the Taupo Volcanic Zone, New Zealand. Other waters may be enriched in lithium, for examples oilfield brines in the Paradox basin, Utah, and in the Smackover Formation in Arkansas and Texas. Brines may be concentrated by evaporation in desert regions. Examples include Clayton Valley, Esmeralda County, Nevada; Searles Lake, California; Great Salt lake, Utah; Salar de Atacama, Chile; Salar de Hombre Muerto, Argentina; and Salar de Uyuni, Bolivia.

Uses

Lithium minerals such as spodumene are used in ceramics, glass, frits and glazes. Lithium metal is used in batteries, nuclear fusion power plants, vitamin-C synthesis, and light-weight high-strength alloys. The metal is used as a deoxidizer and to remove unwanted gases during the manufacture of non-ferrous castings. Lithium vapour is used to prevent carbon dioxide and oxygen from forming scale in furnaces in heat-treating steel. The major industrial use of lithium is in the form of lithium stearate as a thickener for lubricating greases. Lithium carbonate is used in ceramics, pharmaceuticals, and aluminium production, and as a fluxing agent and catalyst; lithium hydroxide is used in alkaline storage batteries and to make lithium salts, greases and soaps; lithium chloride is used in lithium metal production, fluxing, air conditioning and dry batteries; lithium fluoride has various uses in ceramics, optics and glazes; lithium bromide is a drying agent and adsorbent in refrigeration; lithium hydride is used to inflate lifeboats, and its heavy hydrogen (deuterium) equivalent is used in making the hydrogen bomb; butyl-lithium is used in pharmaceuticals, polymerisation and organic synthesis; and lithium-copper and lithium-silver alloys are used as self-fluxing brazing alloys. Lithium is also an essential source for the tritium required in various thermonuclear (fusion) power reactor designs such as the Tokamak where it also serves as a neutron absorber and heat exchanger.

Lithium is increasingly used in lighting, fibreglass, lead crystal and glaze products, and as a substitute for environmentally unfriendly elements such as fluorine.

Name, Formula	Colour	Hardness	Specific gravity	Lustre	Crystal form	Transparency	Fracture
Amblygonite $\text{LiAlPO}_4(\text{F,OH})$	white or grey	5.5-6	3	vitreous-greasy	triclinic	transparent-opaque	conchoidal to uneven, brittle
Eucryptite LiAlSiO_4	colourless, white, tan	6.5	2.65	vitreous	trigonal	transparent	conchoidal, brittle
Lepidolite (lithium mica) $\text{K}(\text{Li,Al})_3(\text{Si,Al})_4\text{O}_{10}(\text{F,OH})_2$	rose red, lilac or white	2.5-3	2.8-3.3	pearly	monoclinic	transparent to translucent	flexible, elastic
Petalite $\text{LiAlSi}_4\text{O}_{10}$	colourless, white, grey, yellow	6-6.5	2.3-2.5	vitreous to pearly	monoclinic	transparent to translucent	subconchoidal, brittle
Spodumene $\text{LiAlSi}_4\text{O}_{10}$	colourless, white, grey, yellowish, greenish	6.5-7.5	3-3.2	vitreous to dull	monoclinic	transparent to translucent	uneven hackley to subconchoidal, brittle
Zinnwaldite $\text{KLiFe}^{+2}\text{Al}(\text{AlSi}_3)\text{O}_{10}(\text{F,OH})_2$	grey, brown	2.5-4	2.9-3.3	vitreous	monoclinic	transparent	flexible, elastic

Table 2: Properties of some lithium minerals.

Price

Prices for lithium minerals in August 1999 were US\$250/t freight on board (fob) for petalite (4.2% Li₂O), US\$385-395/t fob for spodumene (>7.25% Li₂O), and US\$1.00-2.00/lb for lithium carbonate (Industrial Minerals, August 1999; Mining Journal, August 20, 1999).

World production and consumption

Lithium is presently being recovered from brines of Searles Lake, in California, and from those in Nevada. Pegmatite deposits are mined in Australia, Canada, Zimbabwe, China, Brazil and Russia.

World lithium resources are about 2,200 t, 34% are in pegmatites and 66% in brines. Of the pegmatite segment, 33% is spodumene and 1% petalite.

Ore processing

Lithium ores are concentrated from 1-3% Li₂O to 4-6% Li₂O by heavy media separation using dense, nonaqueous liquids, and by froth flotation. The silicate ores are then chemically cleaved by acid or alkaline processes.

In the acid process, spodumene ore is heated in a kiln at a temperature of about 1100°C. After calcining, the ore is mixed with sulphuric acid and roasted at 250°C and then extracted with water to yield a solution of lithium sulphate. Lithium carbonate is recovered by addition of sodium carbonate to the solution after pH adjustment, purification and evaporation. The carbonate is converted to the chloride by reaction with hydrochloric acid.

In the alkaline process, spodumene or lepidolite ores are ground and calcined with limestone at 900-1000°C. The resulting clinker is crushed, milled and extracted with water to yield lithium hydroxide which is converted to the chloride by reaction with hydrochloric acid.

Lithium metal is prepared by the electrolysis of a fused mixture of lithium chloride and potassium chloride in a cell at a temperature of about 400°C.

Lithium is recovered from the brines of Searles Lake, California (<100 ppm Li) by concentration and precipitation as dilithium sodium phosphate. The mixed phosphate is then converted to lithium carbonate, which is the final lithium containing product. Brines from Clayton Valley, Nevada, contain about 200 ppm Li and low concentrations of alkaline earths, simplifying recovery. The lithium is recovered after the brine is concentrated by solar evaporation, and alkaline earths are removed by precipitation. Lithium carbonate is precipitated by the addition of a solution of sodium carbonate to hot brine.

New Zealand occurrence

Lithium is present in dilute brines found in the geothermal fields of the Taupo Volcanic Zone (Fig. 2). Concentrations are typically 10-13 ppm Li, along with higher concentrations of silica, chloride, sodium and potassium. The Wairakei geothermal field alone discharges about 445 t of lithium annually in geothermal waste water, into the Waikato River. In the 1980s, experimental trials were carried out to recover lithium and a variety of other elements including gold, silver, silica, arsenic, cesium and rubidium, from geothermal waters (Roberts, 1986). Before lithium extraction, the waters were pretreated to precipitate out most of the silica.

The lithium was extracted by dosing the brine with sodium aluminate to form lithium aluminate, which was adsorbed on aluminium hydroxide. About 10% of the sodium and potassium present in the water follow the lithium presenting difficulties in further refining and upgrading the lithium into a marketable form. The trials were abandoned as uneconomic at the time.

Future trends

An increase in the use of lithium materials is expected in glassware, rechargeable lithium batteries, fuel cells and other energy-related applications. There is potential for substantial use in the structural metal field, particularly in lightweight alloys.

Magnesium

Discovery and origin of names

Compounds of magnesium have long been known. A small implement made of magnesite was found along with ancient Babylonian glassware and the use of gypsum for mortar was recorded in the first century AD. Black recognised magnesium as an element in 1755. It was first isolated by the British chemist Sir Humphry Davy in 1808, who evaporated the mercury from a magnesium amalgam made by electrolysis a mixture of moist magnesia and mercuric oxide. It was prepared in coherent form by Bussy in 1831.

Magnesium is named after ancient *Magnesia*, a district in Thessaly, Greece. During antiquity, the term magnesia was applied to the soft white mineral steatite, also known as soapstone or talc. Epsom salts were named from the spring discovered at Epsom, England in 1618. N. Grew studied the brine and isolated solid Epsom salt in 1695. Talc is from the Arabic *talq* and was first used by Jahiz of Bassora in 1869. The term steatite, introduced by Pliny the Elder, is from the Greek word *steatos* meaning fat.

Major ores and minerals

Magnesium is the eighth most abundant element in the earth's crust (about 2%). It does not occur in nature as an element, but is found in over 60 minerals such as magnesite, dolomite, brucite, chrysolite and talc (Table 3). Garnierite (Ni,Mg)SiO₃.nH₂O is an ore of nickel. Spinel is a metamorphic magnesium mineral (MgAl₂O₄) sometimes used as a gem. Magnesium is also widely distributed in salt forms, such as magnesium chloride, in sea water, saline-lake and mineral spring waters, and brines. Seawater contains about 0.2 wt % MgO, whereas brines (either naturally occurring or obtained by solution mining of solid salt beds) contain the equivalent of 4-20% MgCl₂. Among the magnesium minerals resulting from evaporation of ocean waters are carnallite (2KCl.MgCl₂.6H₂O), langbeinite (K₂SO₄.2MgSO₄), kieserite (MgSO₄.H₂O), epsomite (MgSO₄.7H₂O), tachyhydrite (2MgCl₂.CaCl₂.12H₂O), and bischofite (MgCl₂.6H₂O).

Properties

Magnesium is one of the alkaline-earth metals of Group IIA of the periodic table. It is a light, silvery-white, and fairly tough metal that is malleable and ductile when heated. Except for beryllium, magnesium is the lightest metal that remains stable under ordinary conditions. It tarnishes slightly in air, and finely divided magnesium readily ignites

Name, Formula	Colour	Hardness	Specific gravity	Lustre	Crystal form	Transparency	Fracture
Bischofite $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	colourless, 1-2 white		1.6	vitreous to dull	monoclinic	transparent to translucent	conchoidal to uneven
Brucite $\text{Mg}(\text{OH})_2$	white, pale 2.5 green, grey, grey-blue, blue		2.4	pearly, waxy or vitreous	trigonal	transparent	plates separable and flexible. Sectile
Dolomite $\text{CaCO}_3 \cdot \text{MgCO}_3$	colourless, 3.5-4 white, greyish, greenish, pale brown, pinkish		2.9	vitreous to pearly	trigonal	transparent to translucent	subconchoidal, brittle
Epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	colourless 2-2.5		1.7	silky to earthy	orthorhombic	transparent	conchoidal
Magnesite MgCO_3	white to 3.5-5 black, grey, blue (crystalline); yellow (cryptocrystalline)		2.9-3	vitreous	trigonal	transparent to translucent	conchoidal, brittle
Periclase MgO	colourless, 5.5 white, grey, yellow, brownish, green, black		3.56-3.58	vitreous	cubic	transparent	
Talc (steatite; soapstone) $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	pale to dark 1 green, white, silvery white, brownish		2.58-2.83	pearly or dull	monoclinic and triclinic	transparent	laminae flexible, inelastic

Table 3: Properties of some magnesium minerals.

upon heating in air and burns with a dazzling white flame. At room temperature, the metal is not attacked by oxygen, water or alkalies, but it is a very strong reducing agent, and reacts with most acids to liberate hydrogen, and displaces hydrogen from boiling water.

The pure metal has low structural strength, so alloys have been developed, principally with aluminium, zinc and manganese, to improve its hardness, tensile strength, resistance to saltwater corrosion, and ability to be cast, welded and machined.

The properties of some magnesium minerals are listed in Table 3.

Formation

Magnesium deposits include deposits of magnesite, seawater and brines, and contact metamorphic deposits of brucite along granite-dolomite contacts (e.g. Malyy Khingan, Russia; Marble Canyon, Texas, USA). Magnesia is produced from surface or subterranean brines in the USA, the Netherlands, Israel and Mexico.

Natural magnesite occurs in a few, but very large, high grade (70-90% MgCO_3) crystalline magnesite deposits and a large number of small, lower grade (>12% MgCO_3) deposits of amorphous or cryptocrystalline magnesite. The crystalline deposits form by replacement of sedimentary dolomite by magnesite, either by hydrothermal alteration or metamorphism. Examples include Veitsch, Styria, Austria; Slovakia; Navarra, Spain; Satka, Russia; Serra des Eguas, Bahia, Brazil; Mount Brussilof, British Columbia, Canada; Gabbs, Nevada, USA; and Jabal Al Rokhan, Saudi Arabia. The amorphous magnesite deposits are formed by alteration of serpentine or allied magnesium-bearing rocks. The

magnesite occurs in veins varying in width from a few millimetres to several metres, and formed by the action of carbon dioxide charged water percolating down or rising up through serpentinised fissures and converting serpentine to magnesite. Examples include Kraubath, Austria; Chalkidhiki Peninsula and Euboea Island, Greece; Kilmar, Quebec, Canada; Liaoning Province, China; Overton, Nevada, and Needles, California, USA; Kunwarara and Marlborough, Queensland; Thuddungra and Fifield, New South Wales; Ravensthorpe, Western Australia; and Khalilovo, Urals, Russia.

Several magnesite deposits in Australia are at an advanced stage of exploration or development, for example Leigh Creek in South Australia (resource of 474 Mt magnesite), and the Arthur River/Lyons River, Savage River and Main Creek deposits in the Arthur Metamorphic Complex of northwest Tasmania.

Uses

About 10% of the magnesium produced is used in metallic form, mostly to prepare light metal alloys. Up to 5% is added to most commercial aluminium. Magnesium is also added to zinc that is to be used for die-casting or in wrought forms, to improve creep strength. The light metal alloys are employed largely for structural purposes where a high ratio of strength to weight is advantageous, including aircraft and automotive parts and in portable tools, luggage trim, materials-handling equipment, artificial limbs, optical instruments and outdoor furniture. The unalloyed metal is used in flashlight photography, flares, and pyrotechnics, incendiary bombs, as a deoxidizer in the casting of metals, and as a getter, a substance that achieves final evacuation in vacuum tubes.

About 90% of magnesium production is used in nonmetallic applications, principally for the production of high temperature refractories. Magnesium carbonate is used as a refractory and insulating material, in pharmaceuticals, glass ceramics, rubber and paints, and fertilizers; magnesium chloride is used as dressing and filler for cotton and woollen fabrics, in paper manufacture, and in cements and ceramics; magnesium citrate is used in medicine and effervescent beverages; magnesium hydroxide is used in medicine as the laxative “milk of magnesia,” in sugar refining, pulp and paper manufacture, and in water treatment; magnesium sulphate is well known as Epsom salt, and is used in pharmaceuticals, chemicals, paper sizing and explosives; magnesium oxide, called burnt magnesia, or magnesia, is used as a heat-refractory and insulating material, in cosmetics, as a filler in paper manufacture, and as a mild, antacid laxative; and organic magnesium compounds (Grignard’s reagents) are used in the production of silicones and other organic compounds, and in the manufacture of titanium.

Price

Magnesium metal prices ranged between US\$2,450 and US\$2,600 per tonne for product containing 99.8% Mg, in August 1999 (Mining Journal, August 20, 1999).

World production and consumption

World production of primary magnesium was 451,500 t in 1998, with production from countries including China (120,000 t), USA (117,000 t), Canada (57,000 t), Norway (49,000 t), Russia (35,000 t), Israel (25,000 t), France (16,000 t), Kazakhstan (10,000 t) and Ukraine (10,000 t).

Magnesium resources are vast. The main sources, dolomite, seawater, brines, salt beds and magnesite, are widely distributed throughout the world. The major deposits of crystalline magnesite are located in the USA, Canada, the CIS, North Korea, China, Greece, Czechoslovakia, Australia, Austria, Brazil, India and Nepal. The total resources are estimated to be about 2800 Mt. The major amorphous or cryptocrystalline deposits are located in Greece, Turkey, Australia and India. The main brine deposits are located in the USA, Mexico, and in the evaporite-salts basin stretching from Scotland to the south of Poland.

Ore processing, smelting and refining

Magnesium is commercially produced by electrolysis of molten magnesium chloride processed mainly from brines, wells and seawater, or by the direct thermal reduction of its compounds with suitable reducing agents, as in the Pidgeon process where calcined dolomite is reduced with ferrosilicon in a retort at 1150°C.

New Zealand occurrence

Magnesite occurs along with talc in ultramafic rocks in Northwest Nelson, Westland, north Otago and Southland (Officers of New Zealand Geological Survey, 1970b; Williams, 1974; Fig. 3).

The Cobb-Upper Takaka district has been a small producer of talc-magnesite for agriculture and industry, but production ceased in the 1980s. Production between 1944-61 totalled 9125 t, mainly for use as fertiliser in the tobacco-growing industry (Coleman, 1966). The largest

producers have been the Takaka #4 lens, which produced 568 t at 60% MgCO₃ in 1967, and the Takaka #2 lens.

The talc-magnesite and quartz-magnesite lenses are derived from serpentinite of the Cobb Igneous Complex outcropping southwards between the Cobb and headwaters of the Takaka River. Wellman (1942), noted four major lenses of magnesite rock, and assessed their grades and resources. In the #1 lens, magnesite content ranged from 44 to 79%, averaging 63%. The lens boundaries are not exposed, but Wellman roughly estimated that it had a length of 500 m and maximum width of 8 m, based on the distribution of surficial float boulders. The larger #2 talc-magnesite lens had a length of 1550 m and maximum width of 220 m, and grades ranged from 35-66%, with most of the material at about 45%. Higher grade material, averaging 70% MgCO₃, was found in the #3 lens, although length and maximum width (590 x 5 m) were less. The #4 lens is the western-most and largest of the four (1740 m length by 820 m maximum width). The lens showed relatively consistent grades of 40-60% MgCO₃, with highest values near contacts with schist.

Wellman (1943) described eight talc deposits hosted in serpentinite of the Cobb Intrusives and located in the head of the Takaka River, in the Waikoromumu River, and in the Parapara River.

Ultramafic bodies containing lenses of serpentinite, talc-magnesite, and steatite within the Waingaro Schist at Richmond Hill, near Collingwood, were investigated by Lime & Marble (Riley, 1972; Thompson, 1989), and four zones, containing lenses up to 200 m in length, were delineated.

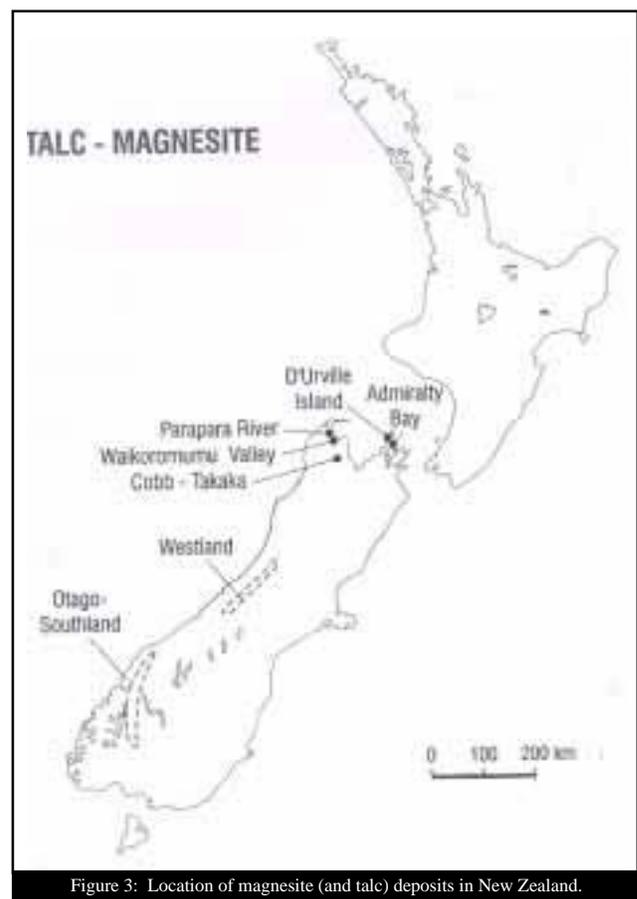


Figure 3: Location of magnesite (and talc) deposits in New Zealand.

Talc-magnesite also occurs along shear zones in the serpentinitic matrix of the Patuki and Croisilles melanges of east Nelson. Although some is of very high grade, the quantities available are small.

Talc-magnesite is present as segregations and veins within serpentinite of the Pounamu Ultramafics (Officers of New Zealand Geological Survey, 1970b). All known deposits are small and poor access is a major limiting factor to potential future development. Most are impure mixtures of talc, calcite, and dolomite, although some are of good quality, locally recrystallised, massive material. The colour is usually grey, but in some cases it has a pale green shade and thin pieces may be translucent. Occurrences include:

- (a) Soapstone Creek on the northern side of the Taramakau River where the main band is 6 m wide and of good quality;
- (b) an un-named northern tributary of the Taramakau River;
- (c) Taipo Gorge where a band of impure talc is up to 15 m wide;
- (d) in the headwaters of Griffin Creek, where several lenses contain good quality, though generally impure, talc;
- (e) between the old serpentine quarry and the summit of Mount Griffin where a talc lens of fair quality is present;
- (f) Whakarira Gorge (Kokatahi River) where rather impure talc comprises a 9 m thick band;
- (g) on Mt Jumbletop where there is a band of impure talc about 6 m wide;
- (h) Nephrite Creek; and
- (i) the McArthur Crags area.

Minor talc-magnesite occurrences are present in ultramafic rocks in northern Otago and Southland.

Production and resources

Both talc and magnesite have been produced from the Cobb deposits for use as a fertiliser, with a total recorded production of 108 t of talc and 21 802 t of magnesite. Last production of magnesite was in 1981 (308 t).

The largest deposit is at Richmond Hill near Collingwood, where four lenses cover more than half a hectare. There is no up-to-date estimate of the quantity or grade.

Future

The use of magnesium is expected to increase in the automobile industry and in steel desulphurisation. Several automobile manufacturers have invested in producing operations to secure a source of magnesium for their products. For example Ford have purchased a magnesium operation in Queensland and Volkswagen have a 35% share of a magnesium plant on the Dead Sea. Auckland Anodisers Ltd have recently developed a new anodising process for magnesium to increase use of magnesium in such items as automobiles, power tools, ladders, sports equipment and bicycles.

Uranium

Discovery and origin of names

Uranium was discovered in 1789 by the German chemist Martin Klaproth, who identified the oxide in uraninite from

Jachymov (Joachimsthal) in the Czech Republic. It was first isolated in the metallic state in 1841 by Eugène-Melchior Péligot by the reduction of uranium tetrachloride with potassium. The radioactive properties of uranium were first demonstrated in 1896 when the French physicist Antoine Becquerel used the fluorescent salt, potassium uranyl sulphate to produce an image on a photographic plate covered with a light-absorbing substance. Otto Hahn and Fritz Strassmann discovered nuclear fission in uranium in 1938. In early 1939, Enrico Fermi suggested that neutrons might be among the fission products and could continue the fission as a chain reaction. This was confirmed by Leo Szilard, Herbert Anderson, Jean-Frédéric Joliot-Curie, and their coworkers. These discoveries led to the first self-sustaining nuclear chain reaction in December 2 1942, the first atomic bomb test in July 16 1945, the first atomic bomb dropped in warfare in August 6 1945, and the first nuclear-powered electrical generator in 1957.

Uranium was named by Klapworth after the then recently (1781) discovered planet Uranus, in turn named after the Greek god *Uranus*, the ruler of the sky or heavens (*Ouranos*). Coffinite, one of the main uranium ore minerals, was named in 1954 after R.C. Coffin, a Colorado Geological Survey staff member. Pitchblende (uraninite) is from the German *pechblende* (*pech* = pitch, *blende* = to deceive). Thucholite was coined in 1928 from the chemical symbols for thorium, uranium, carbon, hydrogen, oxygen + lite, which is from Greek *lithos* for stone.

Major ores and minerals

Uranium metal is unknown in natural settings, as are sulphides, selenides and tellurides. The main ore minerals are the oxides uraninite (pitchblende), coffinite, brannerite and davidite (Table 4). More than 100 secondary (supergene) uranyl (UO₂)²⁺ minerals are known, of which the most common are gummite, schroekingerite, zippeite, autunite, torbernite, carnotite, tyuyamunite and uranophane.

Properties

Uranium has the highest atomic number (90) of the naturally occurring elements. It is one of the actinide series of 14 elements in Group IIIB (Th to Lr) of the periodic table. The actinides are similar in some respects to the lanthanide (rare earth) series of element (Ce to Lu), however, chemically, uranium resembles elements of Group VIB and thus has some marked similarities to chromium, molybdenum and tungsten.

Uranium is a silvery white metal that is malleable, ductile, a little softer than steel, and has a specific gravity of 19. It is slightly paramagnetic and a poor conductor of electricity. It is capable of taking a high polish, but in air, the metal becomes coated with a layer of oxide, and when finely divided it ignites spontaneously (pyrophoric). Uranium is strongly electropositive and, in a finely divided state, reacts with cold water. Acids dissolve the metal, but it is unaffected by alkalis. Uranium has fourteen isotopes, all of which are radioactive. Naturally occurring uranium comprises three radioactive isotopes: 99.275% ²³⁸U, 0.720% ²³⁵U and 0.0054% ²³⁴U. Fission of ²³⁵U releases large amounts of energy. Much of the internal heat of the earth is thought to be attributable to the presence of uranium and thorium.

Name, Formula	Colour	Hardness	Specific gravity	Lustre	Crystal form	Transparency	Fracture
Autunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$	yellow to pale green	2-2.5	3.0-3.2	vitreous	tetragonal	transparent-translucent	
Brannerite $(\text{Y,Ca,Fe,U,Th})_3(\text{Ti,Si})_5\text{O}_{16}$	black	4.5	4.5	vitreous	monoclinic	translucent-opaque	conchoidal
Carnotite $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot x\text{H}_2\text{O}$	yellow to greenish yellow	soft	4.7	dull to earthy	monoclinic		
Coffinite $\text{U}(\text{SiO}_4)_{1-x} \cdot (\text{OH})_{4x}$	black	5-6	5.1	dull to adamantine	tetragonal	opaque	irregular to subconchoidal
Davidite $(\text{Fe,Ce,U})(\text{Ti,Fe,V,Cr})_3 \cdot (\text{O},\text{OH})_7$	black	6	4.3-4.9	submetallic to resinous	trigonal	opaque	subconchoidal to uneven
Euxenite-polycrase $(\text{Y,Ca,Ce,U,Th})(\text{Nb,Ta,Ti})_2\text{O}_6$	dark brown	5.5-6.5	4.3-5.9	submetallic	orthorhombic	opaque	conchoidal
Samarskite $(\text{Y,Ca,Fe,U,Th})(\text{Nb,Ta})_2\text{O}_6$	black	5-6	5.7	resinous, vitreous, submetallic	orthorhombic	opaque	conchoidal
Thucholite $\text{Th,U,C,H}_2\text{O}$	black	3.5-4	1.8	brilliant		opaque	conchoidal, brittle
Torbernite $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$	green	2.5	3.2	vitreous to pearly	tetragonal		
Tyuyamunite $\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot x\text{H}_2\text{O}$	yellow	2	3.7-4.3	adamantine-waxy	orthorhombic	transparent-opaque	
Uraninite (pitchblende) $\text{UO}_2 + (\text{UO}_3, \text{Th}, \text{Pb})$	black-greenish	5-6	7-10	greasy, dull, submetallic	cubic	opaque	conchoidal to uneven, brittle
Uranophane $\text{Ca}(\text{UO}_2)_2\text{Si}_2\text{O}_7 \cdot x\text{H}_2\text{O}$	greenish-yellow	2.5	3.7-3.9	vitreous to greasy	monoclinic	transparent-translucent	brittle

Table 4: Properties of some uranium minerals.

Formation

Deposits of uranium are formed in a wide variety of diagenetic, hydrothermal and weathering processes. The main deposit types are unconformity-related deposits, sandstone uranium deposits, quartz pebble conglomerate deposits, hydrothermal vein deposits and sedimentary breccia deposits described below. In addition, other less important deposit types include intrusive-related deposits (e.g. Rossing in Namibia), collapse breccia pipe deposits (e.g. the Arizona Strip in northern Arizona, USA), contact uranium deposits (e.g. Mary Kathleen, Queensland, Australia), volcanogenic uranium deposits (e.g. Sierra Pena Blanca, Chihuahua, Mexico), and surficial uranium deposits (Yeelirrie, Western Australia) (Eckstrand, 1984; Cox and Singer, 1986; Finch, 1989; Eckstrand *et al.*, 1995).

Unconformity-related vein uranium deposits

Unconformity-related uranium deposits account for about one third of world recoverable resources and current production of uranium. In these deposits, uranium is concentrated along faults and fracture zones at the unconformity between a middle Proterozoic fluvial sandstone sequence and underlying pre-Middle Proterozoic basement metamorphic rocks, such as graphite-mica schist, biotite-garnet schist and dolomitic marble, representing marginal marine sedimentary sequences. Uraninite, coffinite, and hematite occur in stockwork veins, breccias

and replacements forming lenses and pods, typically as flattened cigar-shaped ore bodies. A few deposits contain significant amounts of nickel, cobalt, arsenic and gold. The deposits are typically high grade (0.3-12.0% U) and contain 20,000-200,000 t U. Their genesis is controversial but probably involved syngenetic concentration in the basement host rocks, followed by enrichment during deformation and metamorphism, followed by some late supergene enrichment. Examples include Key Lake, Rabbit Lake, Cluff Lake, McArthur River and Eagle Point in the Athabasca Basin, Saskatchewan, Canada; and Jabiluka I and II, and Ranger I and III in the Pine Creek Geosyncline, Northern Territory, Australia.

Sandstone uranium deposits

Sandstone uranium deposits constitute about 32% of world resources, but their production is declining with the increased importance of unconformity related deposits. Sandstone uranium deposits are formed in fluvial or lacustrine, quartzose sandstones of Mesozoic or Tertiary age. The uranium is transported in oxidised form in groundwater through the permeable clastic rocks and deposited on encountering reducing conditions (carbonaceous matter, sulphides or methane) at a "redox front". Uraninite, coffinite, pyrite and marcasite either fill the pore spaces and matrix or replace organic matter and rock grains unevenly to form tabular and crescent-shaped bodies, that

may have a “c” shaped cross-section - the classic roll front. Individual deposits are mostly in the range of 1000 to 10,000 t of contained uranium in ores grading 0.03 to 0.2% U, but collectively they can form deposits that total more than 100,000 t of contained uranium. Examples include Colorado Plateau, Lucky Mac mine, Wyoming; Jackpile mine, New Mexico; Blizzard, Kelowna, B.C., Canada.

Quartz pebble conglomerate uranium deposits

Quartz pebble conglomerate or pyritic paleoplacer deposits represent about 20% of world uranium resources but production has declined dramatically in the last few years with the closure of mines in Ontario, Canada. These deposits contain uranium-bearing conglomerate and sandstone that were deposited in braided streams and alluvial fans during the Precambrian. The conglomerates are clast supported with well rounded pebbles of quartz, chert, and locally pyrite, in a matrix of quartz, mica, chlorite, pyrite and fuchsite. They contain pyrite, uraninite, brannerite, native gold, and traces of platinum group minerals. A major textural difference from sandstone uranium deposits is the occurrence of the uranium minerals as detrital grains rather than in the matrix. Examples include Blind River-Elliot Lake, Ontario, Canada, the Witwatersrand in South Africa, Jacobina in Brazil and Tarkwa in Ghana. The Blind River-Elliot Lake deposits contain 0.10-0.14% U, little gold and some by-product thorium, whereas the Witwatersrand contains 0.03-0.06% U and yields uranium mainly as a by-product of gold mining.

Sedimentary breccia deposits

Olympic Dam hematitic granite breccia type is a major new type of deposit which was discovered at Olympic Dam, South Australia, in 1975. This single deposit contains an indicated resource of the order of 450 million tonnes at 2.5% Cu, 0.08% U, 0.6 g/t Au and 6.0 g/t Ag, and represents nearly 10% of world uranium resources. The mineralisation is hosted in hematitic granitic breccias of late Precambrian age that were formed by a variety of hydrothermal, magmatic, sedimentary and tectonic processes in a continental rift setting. At Olympic Dam a very large orebody of disseminated chalcopyrite-bornite-chalcocite is accompanied by gold, uranium, silver, rare earths, barium and fluorine minerals. Deposits in Zambia, Zaire, and the Ailik Group in Labrador, Canada, may also belong to this category.

Hydrothermal uranium vein deposits

Hydrothermal uranium vein deposits, also known as Classical uranium vein deposits, represent about 10% of world uranium resources. They are veins, breccias and stockworks associated with steeply dipping fault zones in Proterozoic gneiss, schist and granite. The orebodies range from a few centimetres to a few metres in thickness, rarely up to 15 m, and extend down dip for a few hundred metres, with some deposits in the 1 to 2 km range. The veins contain carbonate and quartz with uraninite, coffinite, and hematite or iron sulphide. Some deposits contain a complex mineralogy grading into the five element (Ag-Ni-Co-As-Bi) vein deposits described in the nickel mineral commodity report (Christie and Brathwaite, 1995b). Classical veins contain 5000-15,000 t U at typical grades of 0.15% to 0.25% U, although grades may be as high as 1% U. Examples include Schwartzwalder, Colorado; Jachymov and Příbram districts, Czechoslovakia; Shinkolobwe, Zaire; and

La Crouzille area, Massif Central, Vendee district, and Armorican Massif in France.

Uses

The main use of uranium is in nuclear reactors to produce about 20% of global electricity from the heat released by nuclear fission reactions.

Manufacture of enriched uranium for use in reactors produces byproduct depleted uranium, a very dense material that has pyrophoric properties on impact. Depleted uranium is used chiefly for armour-piercing projectiles and for counterweights and ballast weights in internal guidance devices, gyro compasses, aircraft control surfaces, and missile reentry vehicles, and as a shielding material. Uranium metal is used for X-ray targets for production of high-energy X-rays; the nitrate has been used as a photographic toner, and the acetate is used in analytical chemistry. Crystals of uranium nitrate are triboluminescent. Uranium salts have also been used for producing yellow “vaseline” glass and glazes.

Price

Uranium oxide (U₃O₈) prices began rising in 1995, after a ten year trend of decreasing prices, and peaked in mid 1996 at US\$16.50/lb. They have since fallen with prices in August 1999 quoted between US\$8.20/lb and US\$10.00/lb (Mining Journal, August 20, 1999). Highest prices were achieved in the late 1970s when prices topped US\$43/lb during the Cold War arms build-up and the oil-price related energy crisis, and the lowest price since that time was in 1991, US\$7.25/lb, because of dumping by the countries of the CIS.

World production and consumption

In 1996, world uranium production was 35,324 t U from 25 producing countries, whereas annual consumption for the more than 400 nuclear reactors currently operating is around 64,000 t U per year, requiring about 29,000 t U draw-down on inventories (Kidd, 1997). This shortfall is met by recycling spent fuel, the draw-down of existing uranium supplies, and blending down of military material. The main producing countries (with 1996 production) include: Canada (11,788 t), Australia (4,974 t), Niger (3,320 t), USA (2,420 t), Russia (2,000 t), Namibia (2,452 t), South Africa (1,440 t), Kazakhstan (1,320 t), Uzbekistan (1,500 t), France (930 t), China (500 t), Gabon (565 t), Czech Republic (600 t), Ukraine (500 t), Spain (225 t), Hungary (200 t), India (200 t), Brazil (125 t), and Romania (100 t) (Kidd, 1997).

“World outside centrally planned economic areas” resources, defined as reasonably assured resources at a cost of <US\$80 per kg U, were estimated at 1.6 Mt U in 1986. About 90% of these resources are in Australia, Brazil, Canada, Namibia, Niger, South Africa and the USA.

Ore processing, smelting and refining

Preliminary treatment of ore may involve a roasting operation, a physical or chemical concentration step, or a combination of these. Chemical concentration involves leaching by either dilute sulphuric acid or sodium carbonate and recovery of uranium as ammonium uranate or sodium uranate (yellow cake) by precipitation with ammonia or with sodium hydroxide. The concentrate is treated chemically to give a uranyl nitrate solution that can be

further purified by solvent extraction to give uranium nitrate crystals. The nitrate serves as a starting material for other compounds, such as oxides. In large-scale processing, the nitrate is decomposed thermally to give UO_3 , which is subsequently reduced with hydrogen to form UO_2 . UF_4 is prepared by treating UO_2 with HF gas. Uranium metal can be prepared from UF_4 by electrolyses of UF_4 in a salt bath or by metallothermic reduction of finely divided UF_4 with calcium or magnesium in steel bombs lined with fused dolomitic oxide (Ames process).

New Zealand occurrence and resources

The main occurrences of uranium in New Zealand are sandstone-type uranium deposits in the lower Buller Gorge and the Pororari River areas, although detrital uraninite has been recorded in gold dredge concentrates at Taramakau River and Gillespies Beach in Westland, and prospecting has identified some radioactive dikes and granites in west Nelson and Fiordland (Officers of the New Zealand Geological Survey, 1970a; Williams, 1974; Brathwaite and Pirajno, 1993; Fig. 4). Uranium minerals found in New Zealand include: autunite, becquerelite, coffinite, ferghanite, gummite, meta-autunite, rutherfordine, sabugalite, schoepite, sklodowskite, torbernite, tyuyamunite, uraninite, uranophane and uranothorite (Railton and Watters, 1990).

Sandstone uranium deposits

Sandstone-type uranium deposits, formed by groundwater leaching of uraniferous granitic source rocks and deposition of uranium in permeable carbonaceous sandstones, are found in the lower Buller Gorge and the Pororari River areas as weak disseminations of coffinite and uraninite in non-marine conglomerate-sandstone beds of Cretaceous

Hawks Crag Breccia and Watson Formation of the Pororari Group. The Hawks Crag Breccia is a coarse angular breccia with thin carbonaceous siltstone and arkosic sandstone beds, and is mainly derived from granite of the Paparoa Range and from the Greenland group greywacke (Tulloch and Palmer, 1990). It is commonly red coloured, due to hematite staining of feldspars. The Hawks Crag Breccia and Watson Formation were deposited in fault angle depressions as alluvial fan and river flood plain deposits.

Tulloch (1988) has related the uranium mineralisation to the circulation of fluids via the Ohika Detachment Fault zone at the contact of the Pororari Group with underlying deformed granite of the Paparoa metamorphic core complex.

Buller Gorge: Bedded uranium deposits are found in the Tirooa Facies of the Hawks Crag Breccia, a mainly granite-derived arkosic facies typically consisting of poorly sorted and matrix-rich, arkosic sandstone, breccia and conglomerate, containing carbonaceous streaks which appear to preferentially host the uranium mineralisation. Uranium mineralisation is found on both the north and south sides of the Buller River, but mineralisation is different in the two areas.

North of the Buller River, at least 10 lensoidal uraniferous horizons up to 60 cm in thickness were identified, however most interest was shown in three horizons (T-J, S-C and Waterfall). Riley (1969) reported grades ranging from 0.89 to 2.34 lbs U_3O_8 per short ton (2000 lb) over mining widths of 1.2 m and over limited strike lengths. Coffinite is the predominant uranium mineral, typically found with carbonate (calcite and ferroan dolomite), pyrite and fluorite (Beck *et al.*, 1958; Wodzicki, 1959). Coffinite is present interstitially to clastic sand grains and pebbles. Thucolite and uraninite are also reported as primary minerals (Williams, 1974). Secondary uranium minerals include autunite, ferghanite, gummite, meta-autunite, rutherfordine, schoepite, sklodowskite, uranophane, saleeite, metatorbernite, tyuyamunite and thucholite (Beck *et al.*, 1958; Riley, 1969; Williams, 1974).

South of the Buller River, and stratigraphically higher in the Hawks Crag Breccia, at least one mineralised lens up to 1.2 m thick is present but continuity along bedding was nowhere proved for more than 90 m (Williams, 1974). The main primary mineral is uraninite and there is a much wider range of associated sulphides such as pyrite and chalcocopyrite (Cohen *et al.*, 1969).

Average grades are up to 0.1% U_3O_8 over a limited section, but are generally much less. The vanadium content is very low at about 0.03%. Beryllium and molybdenum are geochemically anomalous.

Bullock Creek, Pororari River: Some 16 uraniferous zones have been found within the Hawks Crag Breccia and the underlying Watson Formation (Hope *et al.*, 1959; Klaric, 1967; Laird, 1988). In the Hawks Crag Breccia, uranium mineralisation is highly lenticular and is associated with red granite boulders and thin carbonaceous seams. In the Watson Formation (Pororari Formation of Hope *et al.*, 1959), more continuous uraniferous horizons occur in gritty sandstone and siltstone with carbonaceous radioactive seams and interbeds. The primary minerals thucholite and uraninite have been identified. Average grades are in the range of 0.15-0.03% U_3O_8 .

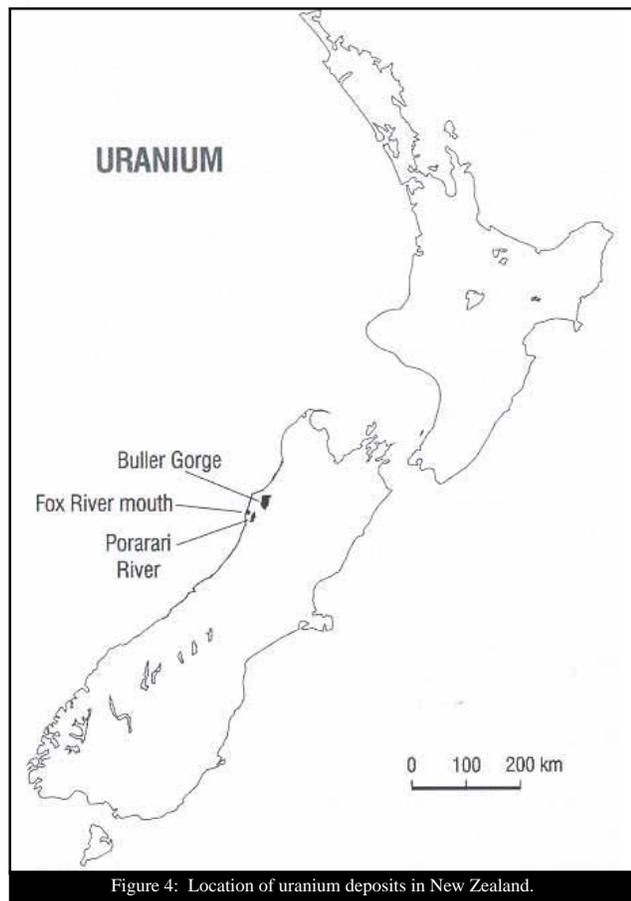


Figure 4: Location of uranium deposits in New Zealand.

CRA found that the uraniferous outcrops were lenticular, small and scattered. Assay results at five localities ranged from 0.46 to 0.82 lb U_3O_8 per short ton (2000 lbs), equivalent to 0.04%. Sample widths ranged from 0.8 to 1.8 m, with outcrop lengths possibly up to 100 m (Riley, 1969).

Subsequent work by Lime & Marble Ltd (Buller Uranium Limited; Riley, 1969) included additional field surveys and the driving and sampling of 35 m adits at two of the CRA localities. Average grades from the two localities were 0.5 and 0.59 lbs U_3O_8 /short ton, calculated over a mining width of 1.2 m, approximately equivalent to 0.025 and 0.03 wt % radiometric. The highest grade obtained was 6.4 lbs (0.32%) over 0.3 m.

Fox River mouth: Carbonaceous streaks that are weakly radioactive (0.2-0.3 R/hr) are found at the southern end of a 300 m long outcrop of leached Hawks Crag Breccia south of the mouth of the Fox River (Beck et al., 1958). Whittle (in Williams, 1974, p. 207) reported sporadic uraninite grains up to 3 mm in diameter, in association with “abundant” chalcopyrite.

Big River: Hope et al. (1959) noted that weak radioactivity had been detected in bedded material consisting of granite cobbles in an arkosic matrix.

Waitahu River: The Hawks Crag Breccia consists of alternating beds similar to the Blackwater facies and Tiroroa “B” facies in the Buller Gorge. Bedding is indistinct, except in places where sandstone bands occur. Low levels of radioactivity have been detected in some beds of the Tiroroa facies.

The Waitahu Breccia occurrence consists mainly of granite fragments of varying size, though a certain amount of hornfelsic sandstone may be seen in some outcrops.

Other occurrences

Occurrences have also been reported from a trachyte dike within Hawks Crag Breccia in Batty Creek (Beck et al., 1958), in a quartz veinlet in granitoids at Sinclairs Castle (Beck et al., 1958), and in hornfels and granite boulders within the Hawks Crag Breccia from Big River and the Buller Gorge (Wodzicki, 1959). At Batty Creek, uranium is concentrated in veins and aggregates of zircon traceable over a distance of more than 40 m, with a maximum grade of 0.28% U_3O_8 . The Big River biotite hornfels boulder described by Wodzicki contained 0.18% U_3O_8 , but the uranium-bearing phase could not be identified. Biotite granite from the same area contained 0.025% U_3O_8 . Biotite hornfels boulders from Batty Creek in the Buller Gorge were strongly radioactive (0.2%), and contained uraninite, the first occurrence identified in New Zealand (Wodzicki, 1959).

Fergusonite and samarskite have been found as rare alluvial grains in the Canaan Valley in west Nelson.

West Coast beach sand

Above average background radioactivity was first detected in blacksand during a wartime search for uranium (Nicholson, 1955) and was later shown to be due to trace concentrations of thorite, uranothorite and monazite in these sands (Hutton, 1950). Measurements of ^{238}U in Barrytown sand by Roberts and Whitehead (1991) indicated concentrations of about 30 ppm (0.003%), about one fifth the concentration of associated thorium. At Gillespies

Beach, the thorite was assayed as 76.6% thorium oxide and the uranothorite as 62.6% thorium oxide and 11.5% uranium oxide (Hutton, 1950). Although no production figures are known, Nicholson (1955) estimated that during gold dredging operations, 0.1 ton of uranothorite was being recovered per week. Based on this estimate and assay figures of Hutton (1950), Caffyn (1971) estimated that 147 pounds of thorium oxide must have been mined each week.

Past production, resources and future potential

There has been no recorded commercial production of uranium from New Zealand deposits and there will be no production in the near future due to New Zealand’s nuclear free legislation and the *Minerals Programme for Minerals other than coal and petroleum* which specifically does not allow prospecting, exploration and mining of the primary uranium and thorium minerals.

Future trends

There is a trend of falling output in countries within the CIS, balanced by a rising output in the major western producing nations. The future use of uranium lies in the continued acceptance of nuclear-powered electricity generation, particularly in countries not enjoying alternative energy sources for producing electricity. Shutdowns of higher-cost reactors and the large-scale introduction of breeder reactors around the year 2010 suggest that there is unlikely to be a major increase in demand for uranium.

Zirconium

Discovery and origin of names

The name zircon probably originated from the Persian word *zargun*, which describes the gold like colour of the gemstone now known as *zircon*, *jargon*, *hyacinth*, *jacinth*, or *ligure*. This mineral, or its variations, is mentioned in biblical writings. The mineral was not known to contain a new element until 1789, when the German chemist Martin Klaproth analysed a jargon from Ceylon and found a new earth, which Werner named zircon (*silex circonius*), and Klaproth called *Zirkonerde* (*zirconia*). The metal was isolated in impure form in 1824 by the Swedish chemist Baron Jöns Berzelius. A higher purity metal was first produced in quantity in 1925 by the Dutch chemists Anton Van Arkel and J.H. de Boer by thermal decomposition of zirconium tetraiodide. In the 1940s, William Kroll of Luxembourg developed his cheaper process of making the metal based on the reduction of zirconium tetrachloride by magnesium.

Major ores and minerals

Zirconium is never found free in nature, but occurs most commonly as zircon ($ZrSiO_4$) and less commonly as baddeleyite (ZrO_2). Hafnium, a metal with properties similar to those of zirconium, is always present in zirconium minerals, with an average Hf:Zr atomic ratio of approximately 0.02, although a few minerals are rich in hafnium (e.g. alvite: Hf, 13.6%; Hf:Zr, 0.54; thortveitite: Hf, 2.7%; Hf:Zr, 1.8). Other common impurities in zircon and baddeleyite include thorium, uranium, rare earths, calcium, magnesium and iron. The U+Th content is detrimental for environmental reasons and degrades the minerals because the radioactive emanations from these elements disorder the lattice structure.

Properties

Zirconium, is one of the transition elements in Group IVb of the periodic table. In its pure state zirconium exists in two forms: the crystalline form, a soft, greyish-white, lustrous, ductile metal; and the amorphous form, a bluish-black powder. When finely divided, the metal may ignite spontaneously in air, especially at elevated temperatures. The solid metal is much more difficult to ignite. Zirconium is exceptionally resistant to corrosion by many common acids and alkalis, by sea water, and by other agents. It is used extensively by the chemical industry where corrosive agents are employed.

Zircon is a transparent, translucent, or opaque mineral, with an adamantine lustre, hardness of 7.5 and a specific gravity of 4.2 to 4.86. Zircon may occur as colourless crystals or in shades of green, grey, red, blue, yellow or brown. The high refractive index and dispersion of zircon cause it to approach diamond in fire and brilliancy. Several varietal names have been applied to coloured gems. The clear, transparent yellow, orange, red and brown varieties are known as hyacinth or jacinth; translucent or opaque varieties, and most of the colourless types, are known as jargon or jargoon. When subjected to high temperatures, zircons either change colour or lose their colour, and assume a greater brilliance. Colourless zircons are known as Matura diamonds or white zircons. A blue variety, produced by heat treatment and known as blue zircon, is also commonly used as a gemstone.

Baddeleyite is a colourless, yellow, green, reddish or brownish black coloured mineral with a greasy to vitreous lustre, subconchoidal to uneven fracture, and is brittle. It has a hardness of 6.5 and a specific gravity of 5.8.

Formation

Zircon occurs as an accessory mineral in all types of igneous rocks and is abundant in silica-rich rocks. It is extremely resistant to weathering and concentrates along with some other heavy minerals in beach and alluvial sand deposits that may contain 0.2-3% of zircon. Zircon is mined as a coproduct of beach sand mining for titanium ores (see titanium mineral commodity report, Christie and Brathwaite, 1998b). The main deposits are the relatively young beach sands found on or near active coast lines of Australia, South Africa, USA, India, Sri Lanka, Malaysia, China, Thailand and Tanzania.

Uses

Most zirconium metal is used in the nuclear power generation industry in cladding, fuel rods, for alloying with uranium, and for reactor-core structures, because of its low neutron-absorption cross section, excellent corrosion resistance, heat resistance, strength, ductility and ease of fabrication. In many of these applications it is used as zircaloy, alloys which contain about 2% tin. Zirconium is also used as an alloying agent in the production of some magnesium alloys and as an additive in the manufacture of certain steels. Other uses include the manufacture of porcelain and ceramics, refractories, explosive primers, flash bulbs, pyrotechnics, as a "getter" in vacuum tubes to remove traces of gases, and in heat exchangers, pump housings, valves, and other equipment subject to corrosion by acids. The chemical applications include adhesives, anti-perspirants, catalysts, and polymers (cross linking/special

fillers). With niobium, zirconium is superconductive at low temperatures and is used to make superconductive magnets. Some zircons are gemstones.

Price

Prices for zircon sand (66-67% ZrO₂) were A\$500-600/t fob in August 1999 (Mining Journal, August 20, 1999).

Ore processing

Zircon and other heavy minerals are concentrated from the beach sands by gravity concentrators and magnetic and high-tension separators. Zirconium is produced by the Kroll process in which zirconium tetrachloride is reacted with magnesium or sodium. When finely powdered zirconium is required, the calcium reduction of ZrO₂ may be used. Hafnium is separated from zirconium by solvent extraction or ion exchange methods.

World production and consumption

Zircon is produced mainly as a byproduct of ilmenite and rutile mining of beach sands in Australia (400,000 t in 1997), South Africa (Richards Bay Minerals 300,000 t in 1997), USA (Florida and Georgia), Brazil and India. Lesser production is from baddeleyite ores at Phalaborwa, South Africa in two different operations: one recovers the mineral as a by-product of open-cast copper mining and another recovers the mineral from phosphate feeds. It is also mined in Rockingham, Perth, Western Australia and Russia's Kola Peninsula.

Deposits of gem zircons are found in Sri Lanka, Madagascar, Norway, and New South Wales, Australia.

New Zealand occurrence and resources

Zircon is widely distributed as an accessory detrital mineral in titanomagnetite and ilmenite beach sand deposits of the North and South islands (see the titanium mineral commodity report, Christie and Brathwaite, 1998b; Fig. 5). Detrital zircon also occurs in alluvial placers in Westland, Otago and Southland.

Ilmenite beach sand deposits near Whitianga and at Wharekawa on the east coast of the Coromandel Peninsula are reported to average 1% zircon (McLaughlin, 1973). If these deposits are ever mined for ilmenite, the zircon would be a potentially recoverable by-product.

The titanomagnetite beach sands on the west coast of the North Island contain trace zircon but few details are known. The Waikato North Head deposit, currently mined for iron ore by BHP New Zealand Steel, contains about 0.1% zircon which is potentially recoverable (Shannon et al., 1965).

The ilmenite beach sands of the West Coast, South Island typically contain 0.1-0.39% zircon, with locally higher concentrations up to 0.5% zircon (McPherson, 1978; Nicholson et al., 1966; Nicholson, 1967; Minehan, 1989). Beach sand at Orepuke, Southland, contains 0.1-1.1% zircon (Martin and Long, 1960).

In Westland, both normal colourless and purple hyacinth varieties of zircon were present in the heavy mineral fraction of concentrates examined by Hutton (1950) from Westland gold dredges working Recent age river gravels at Arahura, Kaniere, Rimu and the Grey River.

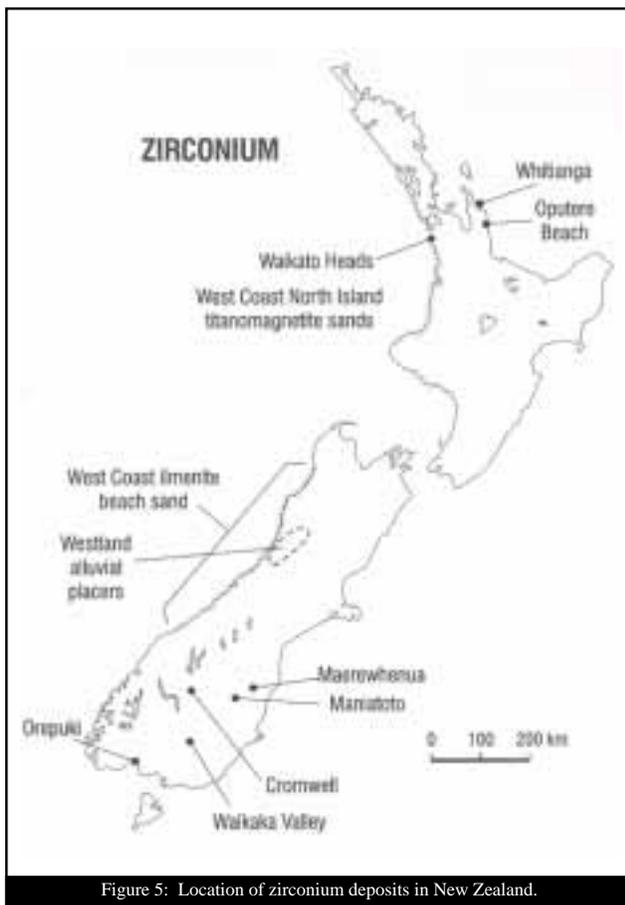


Figure 5: Location of zirconium deposits in New Zealand.

In the Maniototo and Maerewhenua area of North Otago, zircon is conspicuous in the heavy mineral concentrates obtained from most of the Quaternary terrace gravels, sands and auriferous wash. An accumulation of zircon (50-70%) occurs in heavy "grey sand" that accompanied gold concentrates obtained from sluicing in these areas. Dredge concentrate from Lowburn near Cromwell contained abundant zircon (Hutton, 1950). A heavy "grey sand", probably zircon, was reported in sluice boxes of dredges working in Recent age gravels and older quartz pebble drifts of the Waikaka Valley, Southland.

The grade of the zircon in the alluvial gravels is unknown but it is probably well below 0.1%. However it may be worth recovering as a by-product in any future alluvial gold mining operation.

Future trends

There are potential uses of zirconium as a ceramic coating in aircraft engines and other applications where strength and high-temperature oxidation are important. Zircon-based ceramics could be developed for a wide range of uses. Zirconia abrasives could be replaced by synthetic diamond and cubic boron nitride abrasives.

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