

ZIRCONIUM

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Zirconium is a grayish-white, heavy, lustrous metallic element with a high melting point. It is represented by the chemical symbol Zr or the isotopic symbols, Zr^{90} , Zr^{91} , Zr^{92} , Zr^{94} , and Zr^{96} denoting its five naturally occurring isotopes. Zirconium is the 18th most abundant element in the Earth's crust with an average crustal abundance of 165 parts per million. The element was discovered in Germany by Martin Heinrich Klaproth in 1789 by analyzing zircon, although the mineral and gemstone had been known since ancient times (Weeks and Leicester, 1968). Production of the first impure zirconium metal was by Jons Jakob Berzelius in 1824. Commercial metal production is by reduction of zirconium tetrachloride with magnesium using the Kroll process. Zirconium oxide, also called zirconia, has the fifth highest melting point of the binary oxides.

Hafnium is a bright silver, ductile, lustrous metallic element with a very high melting point. It is represented by the chemical symbol Hf or the isotopic symbols, Hf^{174} , Hf^{176} , Hf^{177} , Hf^{178} , Hf^{179} , and Hf^{180} denoting its six naturally occurring isotopes. Hafnium is the 45th most abundant element in the Earth's crust with an average crustal abundance of 3 parts per million. The element was discovered in 1923 by Dirk Coster and George Charles von Hevesey by separation from zirconium (Weeks and Leicester, 1968). Metal was first produced in 1925 by Anton Eduard van Arkel and Jan Hendrik deBoer by passing hafnium tetrachloride over a tungsten filament (van Arkel and de Boer, 1925). Commercial metal production is by reduction of hafnium tetrachloride with magnesium using the Kroll process. Hafnium oxide, also called hafnia, has the second highest melting point of the binary oxides.

The zirconium silicate mineral, zircon ($ZrSiO_4$), is the primary naturally occurring material of economic significance. Baddeleyite, a natural form of zirconia (ZrO_2), is secondary to zircon in its economic significance. Zirconium and hafnium are both contained in zircon at a ratio of about 50:1. Zircon is a coproduct or byproduct of the mining and processing of heavy-mineral sands for the titanium minerals, ilmenite and rutile, or tin minerals. The major end uses of zircon are refractories, foundry sands (including investment casting), and ceramic opacification.

World production of zirconium mineral concentrates was estimated to have decreased slightly in 1997. Data on U.S. production and consumption of zircon concentrates were withheld to avoid disclosing company proprietary data. Domestic production of milled zircon increased slightly in 1997. According to U.S. Customs trade statistics, the United States was a net importer of zirconium ore and concentrates. However, during 1997 the United States was less import reliant than in 1996. Imports of zirconium ore and concentrates decreased significantly as a new mine started production in Virginia. U.S. exports of zirconium ore and concentrate increased 27%.

With the exception of prices, all data in this report have been rounded to three significant digits. Totals and percentages were calculated from unrounded numbers.

Production

Data for zirconium and hafnium materials are developed by the U.S. Geological Survey from one voluntary survey of domestic operations. Of the 33 operations surveyed, 27 responded. Data for nonrespondents were estimated based on prior year levels. Data on domestic production and consumption of zircon concentrates were withheld to avoid disclosing company proprietary data. Milled zircon production increased by 345 metric tons in 1997, while zirconium oxide production increased by 875 tons. (See table 1.)

Zircon is normally produced as a byproduct of the mining and processing of heavy-mineral sands for the titanium minerals rutile and ilmenite. U.S. mine producers of zircon in 1997 were RGC (USA) Mineral Sands, Inc. and E.I. du Pont de Nemours and Co. (DuPont). DuPont produced zircon from its heavy-mineral sands deposits near Starke, FL. RGC (USA) Mineral Sands, Inc. produced zircon from its operations at Green Cove Springs, FL, and Stony Creek, VA. U.S. producers of zirconium and hafnium metal were Wah Chang, Albany, OR, and Western Zirconium, Ogden, UT. Primary zirconium chemicals were produced by Wah Chang and Magnesium Elektron Inc., Flemington, NJ. Secondary zirconium chemicals were produced by about 10 companies, and zirconia was produced from zircon sand at plants in Alabama, New Hampshire, New York, Ohio, and Oregon.

RGC completed construction of production facilities at the Old Hickory heavy-mineral sands deposit at Stony Creek, VA. The mine opened October, 21, 1997, with an expected mine life of 17 years. The \$49 million investment for mine and facilities development created 70 jobs, with an additional 25 jobs generated through contracted support (Commonwealth of Virginia, 1997). When fully operational, RGC expects the mine to produce up to 30,000 metric tons per year of zircon (Mineral Sands Report, 1997).

Consumption

Approximately 95% of all zirconium consumed is in the form of zircon, zirconium oxide, or other zirconium chemicals. The remainder is consumed as zirconium metal and zirconium-containing alloys.

Zircon, used for facings on foundry molds, increases resistance to metal penetration and gives a uniform finish to castings. Milled or ground zircon is used in refractory paints for coating the surfaces of molds. Zircon, in the form of refractory bricks and blocks, is used in furnaces and in hearths for containing molten metals. Glass tank furnaces use fused cast and bonded alumina-zirconia-silica-base refractories. Baddeleyite is used principally in the manufacture of alumina-zirconia abrasives, but also is used in ceramic colors and refractories.

Stabilized zirconium oxide exhibits high light reflectivity and good thermal stability and is primarily used as an opacifier and pigment in

glazes and colors for pottery and other ceramic products. Yttria-stabilized zirconia (YSZ) is used in the manufacture of oxygen sensors that control combustion in furnaces and automobile engines. YSZ is also used in the manufacture of a diverse array of products including high-temperature high-strength structural ceramics, coatings for the hot sections of jet engines, and cubic zirconia, a gemstone simulant.

Because of its low thermal neutron absorption cross section, hafnium-free zirconium is used as cladding for nuclear fuel rods. Commercial-grade zirconium, unlike nuclear grade, contains hafnium and is used in the chemical process industries because of its excellent corrosion resistance. Hafnium is used in nuclear control rods because of its high thermal neutron absorption cross section. However, the largest end use for hafnium metal is as an alloy addition in superalloys.

Prices

In 1997, the tight supply of zirconium-based concentrates continued to cause prices to increase. The average value of imported ore and concentrates increased from \$391 per metric ton in 1996 to \$446 per metric ton in 1997, an increase of 14%. Domestic prices of standard-grade zircon were unchanged, primarily the result of a decrease in the value of the Australian dollar against other major foreign currencies, including the U.S. dollar. Published prices for imported grades of zircon were either slightly higher or unchanged from 1996. Published prices for zirconium, hafnium, and zirconium oxide products were unchanged. (*See table 2.*)

Foreign Trade

According to the U.S. Bureau of the Census trade statistics, the United States was a net importer of zirconium ore and concentrates in 1997. U.S. imports of zirconium ore and concentrates were 62,400 tons, a decrease of 30,100 tons from those in 1996. Australia and South Africa supplied about 98% of the imports of ores and concentrates. U.S. exports of zirconium ore and concentrates were 44,300 tons.

The United States was a net exporter of zirconium and hafnium metal in 1997. Imports of unwrought zirconium metal and waste and scrap were 688 tons, an 11% increase compared with those of 1996. The leading import sources of unwrought zirconium, in order of quantity, were France, Germany, and Austria. U.S. exports of unwrought zirconium metal and waste and scrap were 139 tons, a 2% increase in tonnage compared with those of 1996. U.S. exports classified as other zirconium metal, waste and scrap were 1,080 tons.

Domestic imports of ferrozirconium alloys were 84.3 tons in 1997. Imports originated from Brazil, Russia, and the United Kingdom.

U.S. imports of unwrought hafnium metal and waste and scrap were 6.96 tons, a 12% decrease compared with those of 1996. (*See tables 3 and 4.*)

World Review

Excluding U.S. production, world production of zirconium mineral concentrates in 1997 is estimated to be 926,000 tons, a decrease of less than 1% compared with that of 1996. (*See table 5.*) Australia and South Africa supplied about 85% of all production outside the United States. World reserves of zircon are estimated to be 36

million tons ZrO_2 , while identified world resources of zircon exceeded 60 million tons ZrO_2 . During 1997, the zirconium industry was active in the exploration and development of mineral deposits on a global basis, particularly in Australia, Kenya, Mozambique, and South Africa.

Australia.—Australia is the largest producer of zircon concentrates in the world. In 1997, major producers of zircon concentrates were RGC Ltd., Westralian Sands Ltd. (WSL), Tiwest Joint Venture, Cable Sands Ltd. (CSL), and Consolidated Rutile Ltd. (CRL). Official estimates of zircon production decreased about 16% from those of 1996, the result of declining ore grades and the closure of CSL's Waroona Mine in Western Australia (Australian Mineral Statistics, 1998).

BHP Titanium Minerals (formerly Mineral Deposit Ltd.) produced minerals from its three mines at Viney Creek and Fullerton, New South Wales, and from its Beenup operation in Western Australia. Exports of heavy-mineral sands, including zircon commenced from Beenup in 1997. Dredging at Beenup processed up to 3,500 tons of ore per hour. Zircon capacity at Beenup is 20,000 tons per year. BHP's New South Wales operations at Viney Creek processes up to 2,500 tons per hour and its Fullerton plant operates at up to 1,200 tons per hour. Wet concentrate from the two New South Wales mines is processed at the Hawks Nest dry separation plant (BHP Titanium Minerals, accessed May 21, 1998, at URL <http://www.bhp.com.au/aboutbhp/fastfacts/titanium.htm>).

BHP Titanium Minerals Pty. Ltd.'s Beenup project in Western Australia was commissioned in early 1997. At full capacity, the dredging operation was expected to process 3,500 tons per hour. The dry plant capacity was expected to produce 600,000 tons per year of ilmenite and 20,000 tons per year of zircon. Shipments of heavy-mineral concentrates began in 1997 (Broken Hill Proprietary Company, 1997). The Beenup Mine reportedly operated significantly below capacity levels in 1997 due to startup problems. Zircon production from the Beenup Mine was negligible (Minerals Sands Report, 1998a).

Tiwest Joint Venture, an Australian collaboration of Kerr-McGee Corp. (USA) and Minproc Holdings, operated a heavy-mineral sands mine at Cooljarloo, Western Australia. Reserves at the deposit were 177 million tons of sands grading 3.7% heavy minerals. The economic heavy-mineral fraction of the sands grades 4.5% rutile, 61.3% ilmenite, 3.3% leucogene, and 11.1% zircon. Production in 1997 was 234,000 tons of heavy minerals, an increase of 57% from 1996, but essentially the same as in 1995 (Kerr-McGee Corp., 1997). Zircon production was reportedly 62,000 tons, a 40% increase over 1996 production (Mineral Sands Report, 1998b).

RGC Ltd. discovered two heavy-mineral sands deposits near Ouyen in northwestern Victoria. The onshore deposits, containing ilmenite, rutile, and zircon, are in ancient beach strand lines covered by 15 to 30 meters of sediments. The heavy mineral ore zone is reportedly 5 to 10 meters thick, up to 120 meters wide, and tens of kilometers in length (The University of Adelaide, Geology Honours Project Topics for 1998, accessed June 4, 1998, at URL http://geology.adelaide.edu.au/hons_98.html).

CRL moved the dredge and floating concentrator from its exhausted Bayside deposit to its Ibis-Alpha heavy-mineral deposit on North Stradbroke Island. During the transition, the plant was upgraded to process up to 3,000 tons of sand per hour. Zircon production in 1997 was reportedly 55,000 tons, an increase of 39% over 1996. Both CRL dredges reportedly operated at full capacity

during the year (Mineral Sands Report, 1998a).

WSL reported production of 38,000 tons of zircon, a 31% decrease from 1996. Decreased ore grades in the current mining area was the primary reason for the decline. Zircon production was expected to increase in 1998 as a result of increased processing of ilmenite (Mineral Sands Report, 1998c).

CSL ceased production at its Waroona Mine in Western Australia at midyear. The plant was moved to its Yarloop deposit, 55 kilometers northeast of Bunbury. CSL also produced concentrate from its Jangardup Mine. Zircon production at CSL was estimated to have decreased 10% to 36,000 tons (Mineral Sands Report, 1998d).

India.—Indian Rare Earths Ltd. announced the opening of a new zirconia powder plant at Chavara. The plant has a 500-ton-per-year capacity with a planned expansion to 1,200 tons per year as market conditions warrant. The plant's primary product will be a 1 to 1.2 micron powder for the ceramic glaze market (Industrial Minerals, 1997b).

Japan.—Tosoh Corp. increased its zirconia powder capacity from 270 to 370 tons per year. Zirconia powder is produced by Tosoh from zircon sand through a batch process of hydrolysis followed by calcining, milling, and spray drying. Increased demand for zirconia powder by the electronics industry was cited as the driving force for the expansion (Industrial Minerals, 1997a).

Kenya.—Tiomin Resources Inc., based in Toronto, Canada, identified several mineral sands deposits in 1996. Tiomin acquired an 80% interest in the licensed mineral rights for prospecting areas along the Kenyan coast, while Pangea Goldfields Inc. retained the remaining 20% interest. According to Tiomin, a resource of 2 billion tons grading 3% heavy minerals has been defined by preliminary drilling and sampling. In 1996, Tiomin commenced a drilling program on the Mamburi, Sokoke, Kwale, Mombasa, and Sabaki deposit areas (Tiomin Resources Inc., 1997). Of the five deposits, the Kwale is the most advanced with reserves reported at 200 million tons of heavy minerals with a cutoff grade of 1%. A prefeasibility study of Kwale was completed indicating a \$96 million investment to bring the deposit into production (Tiomin Resources Inc., accessed June 3, 1998, at URL <http://www.smart-globalinvestor.com/Companies/Tiomin.html>).

Korea, Republic of.—Geologists from Choongnam University discovered a large mineral sands deposit at Sanchung-Myon, Hadong-Koon, Kyungnam Province.

Norway.—The joint venture of BM Trading (45%), Kovdor Mining (30%), and the Cookson Group (25%) began operation of a baddeleyite plant at Narvik. Baddeleyite for the plant is sourced as a byproduct from Kovdor's apatite and magnetite mine on Russia's Kola Peninsula. The joint-venture operations include a smelting plant to produce zirconia and crushing, screening, and milling facilities to produce various grades of milled zirconia. Both monoclinic and calcia-stabilized zirconia products are planned (Industrial Minerals, 1997c).

Russia.—Kovdor's apatite and magnetite mine on the Kola Peninsula continued to produce baddeleyite for domestic and foreign use. Kovdor reportedly produced 4,500 tons of baddeleyite in 1996 for export and was expected to produce 5,000 tons for shipment in 1997.

South Africa.—South Africa is the second largest source of zirconium minerals production in the world. Zirconium minerals are produced from three sources. Heavy-mineral mining operations of

Namakwa Sands Ltd. and Richards Bay Minerals yield zircon concentrates, while baddeleyite is produced at Palabora as a byproduct of open pit copper and phosphate mining.

Namakwa Sands Ltd. started construction of a second ilmenite smelter. To supply feed to the additional smelter, Namakwa planned to expand ilmenite production, with a corresponding increase in coproduct zircon output. Zircon capacity from the Brand-se-Baai Mine and Koekenaap separation plant near Vrendal/Lutzville is expected to increase from 56,000 tons to 140,000 tons per year (Industrial Minerals, 1997d).

The Palabora Mining Company Ltd. reported production of 9,293 tons of baddeleyite concentrates (grades 1, 2, and 3) in 1997, a decrease of 13.9% compared with that of 1996. Production of zirconium sulfate tetrahydrate (ZST) was 2,151 tons, a decrease of 20%. Production of grade 5 baddeleyite, a ceramic pigment grade, increased 4.6% over 1996 to 2,054 tons. The mine produced 30.8 million tons of ore in 1997, a 7% decrease from last year. Palabora improved its mining efficiency by installing an in-pit crusher to minimize the volume of ore hauled (Palabora Mining Company Ltd., 1997).

Iscor Limited completed its environmental management program and continued with development of its KwaZulu-Natal heavy-mineral deposit (Iscor Limited, 1997). When completed, capacity at the Hillendale mine is expected to include 35,000 tons per year of zircon.

Gencor Limited reported that Richards Bay Minerals increased its revenues 83% to R\$451 million. The improvement was the result of higher mineral sands prices, higher sales, and the weakening of the Rand against other foreign currencies (Gencor Limited, 1997).

Outlook

Global demand for zirconium materials is expected to increase by 3% annually over the next few years. A relatively tight supply of zircon resulted in increased prices of zirconium products in 1996 and 1997. Over the next few years, however, the supply and demand of zircon is expected to be in closer balance as new deposits and plant expansions come on-line. Expansions in supply are expected in Mozambique, South Africa, and the United States, while further exploration and development efforts are likely in India, Kenya, and the Ukraine.

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TABLE 1
SALIENT U.S. ZIRCONIUM STATISTICS 1/

(Metric tons)

	1993	1994	1995	1996	1997
Zircon:					
Production:					
Concentrates	W	W	W	W	W
Milled zircon	46,700	53,300	56,000	55,300	55,700
Exports	35,900	32,000	40,300	35,000	44,300
Imports for consumption 2/	70,000	82,000	93,600	92,500	62,400
Consumption, apparent 2/	W	W	W	W	W
Stocks, December 31: Dealers and consumers 3/	26,000	30,100	33,400	34,300 r/	26,800
Zirconium oxide:					
Production 4/	10,000	12,100	14,200	15,000	15,900
Exports 5/	1,280	1,220	1,680	1,480	1,970
Imports for consumption 5/	1,990	2,400	4,370	5,240	4,220
Consumption, apparent	NA	W	W	W	W
Stocks, December 31: Producer 4/	719	W	W	822 r/	698

r/ Revised. NA Not available. W Withheld to avoid disclosing company proprietary data.

1/ Data are rounded to three significant digits.

2/ Includes insignificant amounts of baddeleyite.

3/ Excludes foundries.

4/ Excludes intermediate oxides associated with metal production.

5/ Includes germanium oxides and zirconium dioxides.

TABLE 2
PUBLISHED YEAREND PRICES OF ZIRCONIUM AND HAFNIUM MATERIALS

Specification of material	1996	1997
Zircon:		
Domestic, standard-grade, f.o.b. Starke, FL, bulk, per short ton 1/	\$419.00	\$419.00
Domestic, 75% minimum quantity zircon and aluminum silicates, Starke, FL, bulk, per short ton 1/	381.00	381.00
Domestic, premium-grade zircon, Starke, FL, bulk, per short ton 1/	489.00	489.00
Imported sand, ceramic application, f.o.b., bulk, per metric ton 2/	\$410.00 - 440.00	\$420.00 - 470.00
Imported sand, refractory application, f.o.b., bulk, per metric ton 2/	390.00 - 425.00	390.00 - 425.00
Imported sand, foundry sand application, f.o.b., bulk, per metric ton 2/	380.00 - 420.00	380.00 - 420.00
Baddeleyite, imported concentrate: 3/		
98% to 99% ZrO ₂ , minus 100-mesh, c.i.f. Atlantic ports, per pound	.91	.98
Over 99% ZrO ₂ , minus 100-mesh, c.i.f. Atlantic ports, per pound	1.13	1.43
Zirconium oxide: 4/		
Powder, commercial-grade, drums, 2,000-pound minimum, per pound	3.00 - 6.60	3.00 - 6.60
Electronic, same basis, per pound	3.50 - 8.00	3.50 - 8.00
Insulating, stabilized, 325° F, same basis, per pound	3.35 - 4.00	3.35 - 4.00
Insulating, unstabilized, 325° F, same basis, per pound	3.35 - 4.00	3.35 - 4.00
Dense, stabilized, 300° F, same basis, per pound	3.60	3.60
Zirconium: 5/		
Powder, per pound	75.00 - 150.00	75.00 - 150.00
Sponge, per pound	9.00 - 12.00	9.00 - 12.00
Sheets, strip, bars, per pound	20.00 - 50.00	20.00 - 50.00
Hafnium, sponge, per pound 5/	75.00 - 95.00	75.00 - 95.00

1/ E. I. du Pont de Nemours & Co. Inc. price list, July 1, 1996, and July 1, 1997, respectively.

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TABLE 3
U.S. EXPORTS OF ZIRCONIUM, BY CLASS AND COUNTRY 1/

Class and country	1996		1997	
	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)
Ore and concentrates:				
Argentina	234	\$272	487	\$91
Belgium	672	390	356	200
Brazil	1,590	706	3,620	1,850
Canada	7,920	3,780	5,530	3,010
China	349	474	3,320	2,450
Colombia	1,800	2,050	2,200	2,130
Dominican Republic	255	303	198	235
Ecuador	127	147	119	101
France	1,090	836	1,060	844
Germany	8,420	4,320	2,980	2,100
Hong Kong	1,560	1,660	702	626
Indonesia	429	519	487	376
Ireland	114	134	123	144
Italy	166	114	100	70
Japan	268	102	1,180	424
Korea, Republic of	347	251	181	128
Malaysia	136	159	390	303
Mexico	5,110	2,420	4,150	2,020
Netherlands	--	--	3,640	582
Pakistan	20	15	312	257
Philippines	78	92	331	281
Singapore	215	272	--	--
Spain	276	269	3,080	410
Sweden	528	259	53	26
Taiwan	195	206	448	286
United Kingdom	1,330	1,040	7,680	2,970
Venezuela	1,480	1,650	1,010	798
Other	338	324	594	452
Total	35,000	22,800	44,300	23,200
Unwrought zirconium and waste and scrap:				
Japan	32	713	63	781
United Kingdom	41	1,250	30	860
Other	64	1,580	46	1,200
Total	136	3,550	139	2,840

1/ Data are rounded to three significant digits; may not add to totals shown.

Source: Bureau of the Census.

TABLE 4
U.S. IMPORTS FOR CONSUMPTION OF ZIRCONIUM AND HAFNIUM, BY CLASS AND COUNTRY 1/

Class and country	1996		1997	
	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)
Zirconium ore and concentrates:				
Australia	44,500	\$15,000	26,400	\$10,400
South Africa	47,100	19,700	35,000	14,700
Other	943	1,530	957	2,650
Total	92,500	36,200	62,400	27,800
Zirconium, unwrought and waste and scrap:				
Austria	--	--	60	302
Canada	117	1,630	26	1,830
China	--	--	49	443
France	309	23,100	384	13,400
Germany	46	7,770	66	11,600
Japan	44	1,690	40	1,690
Netherlands	37	2,480	4	126
Russia	--	--	29	216
United Kingdom	28	161	(2/)	10
Other	38	922	30	1,150
Total	619	37,800	688	30,700
Hafnium, unwrought and waste and scrap:				
Australia	(2/)	32	--	--
France	7	1,190	6	1,020
Germany	1	311	(2/)	270
United Kingdom	(2/)	46	(2/)	3
Total	8	1,580	7	1,290

1/ Data are rounded to three significant digits; may not add to totals shown.

2/ Less than 1/2 unit.

Source: Bureau of the Census.

TABLE 5
ZIRCONIUM MINERAL CONCENTRATES: WORLD PRODUCTION, BY COUNTRY 1/ 2/

(Metric tons)

Country	1993	1994	1995	1996	1997 e/
Australia	414000	511000 r/	518000 r/	502000 r/	424000 3/
Brazil 4/	13252	17064	16343	17000 r/	17000
China e/	15000	15000	15000	15000	15000
India e/	17000	18000	18000	19000	19000
Indonesia e/	2500	2500	2000	2000	2000
Malaysia	2184	1656	3790	4511 r/	2500
Russia e/ 5/	2500	3000 r/	4000 r/	4500 r/	5000
Sierra Leone e/	1200	1300	--	--	--
South Africa e/ 6/	243000	226000	250000	300000 r/	360000
Sri Lanka	14401	22310	21971 r/	15863 r/	16000
Thailand	707	326	--	--	--
Ukraine e/	70000	65000	60000	55000	65000
United States	W	W	W	W	W
Total	796000	883000 r/	909000 r/	935000 r/	926000

e/ Estimated. r/ Revised. W Withheld to avoid disclosing company proprietary data.

1/ World totals and estimated data are rounded to three significant digits; may not add to totals shown.

2/ Includes data available through June 18, 1998.

3/ Reported figure.

4/ Includes production of baddeleyite-caldasite.

5/ Includes production of baddeleyite.

6/ Includes production of byproduct zircon from titanium sands mining and 10,000-15,000 tons per year baddeleyite from Palabora Mining Co. Ltd.