

ME551/GEO551 Geology of
Industrial Minerals
Spring 2014

Commodities, Part 5



Manganese, nepheline syenite,
silica, strontium, sodium sulfate,
talc, trona (soda ash), niobium,
zeolites, zircon

Schedule

- project presentations next Wed
- This weekend potash mine, Carlsbad
- Final and project report due May 10

Introduction

- Manganese (Mn) was discovered by Scheele and isolated by Gahn in 1774
- A silver–gray metal, resembling iron but harder and more brittle
- Forms 0.09% of earth's crust
- Atomic Number : 25
- Relative Atomic Mass : 55
- Melting Point : 1245°C
- Boiling Point : 2150°C
- Relative Density : 7.43
- Hardness on Mohs scale: 5.0



[www.theodoregray.com/
PeriodicTable/Elements/027/](http://www.theodoregray.com/PeriodicTable/Elements/027/)

Manganese Minerals

- Mn does not occur in nature as a native metal, but in over 100 minerals including, oxides, carbonates and silicates

Mineral	Chemical Composition	% Mn
Hausmanite	Mn_3O_4	72
Polianite	MnO_2	63.1
Pyrolusite	MnO_2	60-63
Cryptomelane	$KR_8O_{16}R$ (R=Mn)	Variable
Psilomelane	$BaMn Mn_8O_{16}(OH)_4$	45-60
Coronadite	$PbR_8O_{16}R$ (R=Mn)	Variable
Hollandite	$BaR_8O_{16}R$ (R=Mn)	Variable
Manganite	$Mn_2O_3 \cdot H_2O$	62
Braunite	$3Mn_2O_3 \cdot MnSiO_3$	62
Tephroite	$2MnO \cdot SiO_2$	54.3
Rhodochrosite	$MnCO_3$	47
Rhodonite	$MnSiO_3$	42
Spessartite	$3MnO \cdot Al_2O_3 \cdot 3SiO_2$	33.3
WAD	Hydrous Mn Oxides	Variable
Franklinite	$(Fe, Mn, Zn)O(Fe, Mn)_2O_3$	Variable
Asbolan	Cobaltiferous WAD	Variable
Alabandite	MnS	63.14

Commonly Mined Mn Minerals

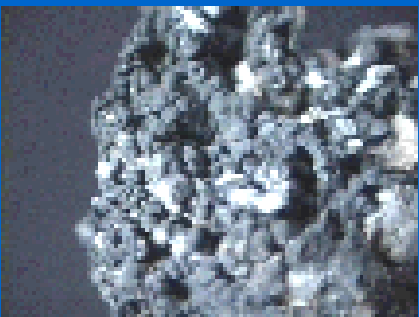


Pyrolusite (MnO_2)

Rhodochrosite (MnCO_3)



Psilomelane [$(\text{BaH}_2\text{O})_2\text{Mn}_5\text{O}_{10}$]



Geology of Mn ores

- Occurs worldwide in various geological environments
- Two major types of economic Mn ore deposit
 - Sedimentary deposits
 - Residual deposits
- Minor type of ore deposit
 - Metamorphic deposits

Geology of Mn ores

- Sedimentary deposits
 - the most common, usually stratiform or lenticular. Formed by chemical processes during the deposition of marine sediments. Contain manganese oxides and carbonate minerals, interbedded together or with limestone or shale
- Residual deposits
 - formed by alteration of existing manganese deposits or by concentration of the manganese minerals when other minerals are washed away by weathering or ground water processes
- Metamorphic deposits
 - regionally metamorphosed sedimentary or residual deposits, occurring in marbles, slates, quartzites, schists, and gneisses

Manganese Nodules

- Potato-size chunks of Mn mixed with Fe, Ni, Co and other useful metals
- Exist in deep ocean floors: e.g., at depths between 14,000ft and 17,000ft in the Pacific ocean
- Deep Ocean Mining Project
 - Howard Hughes built *Glomar Explorer* at a cost of over \$200 mil, funded by CIA, to retrieve a Soviet submarine on June 20, 1974.
 - The Soviet Golf-II Class ballistic missile submarine had sunk on April 11, 1968, ~750 miles northwest of Hawaii
 - (Miners News, Vol. 20, Issue 1)
- Manganese nodules have not been mined yet



[www.theodoregray.com/
PeriodicTable/Elements/02
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[http://www.fas.org/irp/program/
/collect/jennifer.htm](http://www.fas.org/irp/program/collect/jennifer.htm)

Major World Mn Deposits

The World

Nikopol, Ukraine and Tchiatoura, Russia

S. Appalachian, U.S.

Franklin, NJ

Nsuta, Ghana

Moanda, Gabon

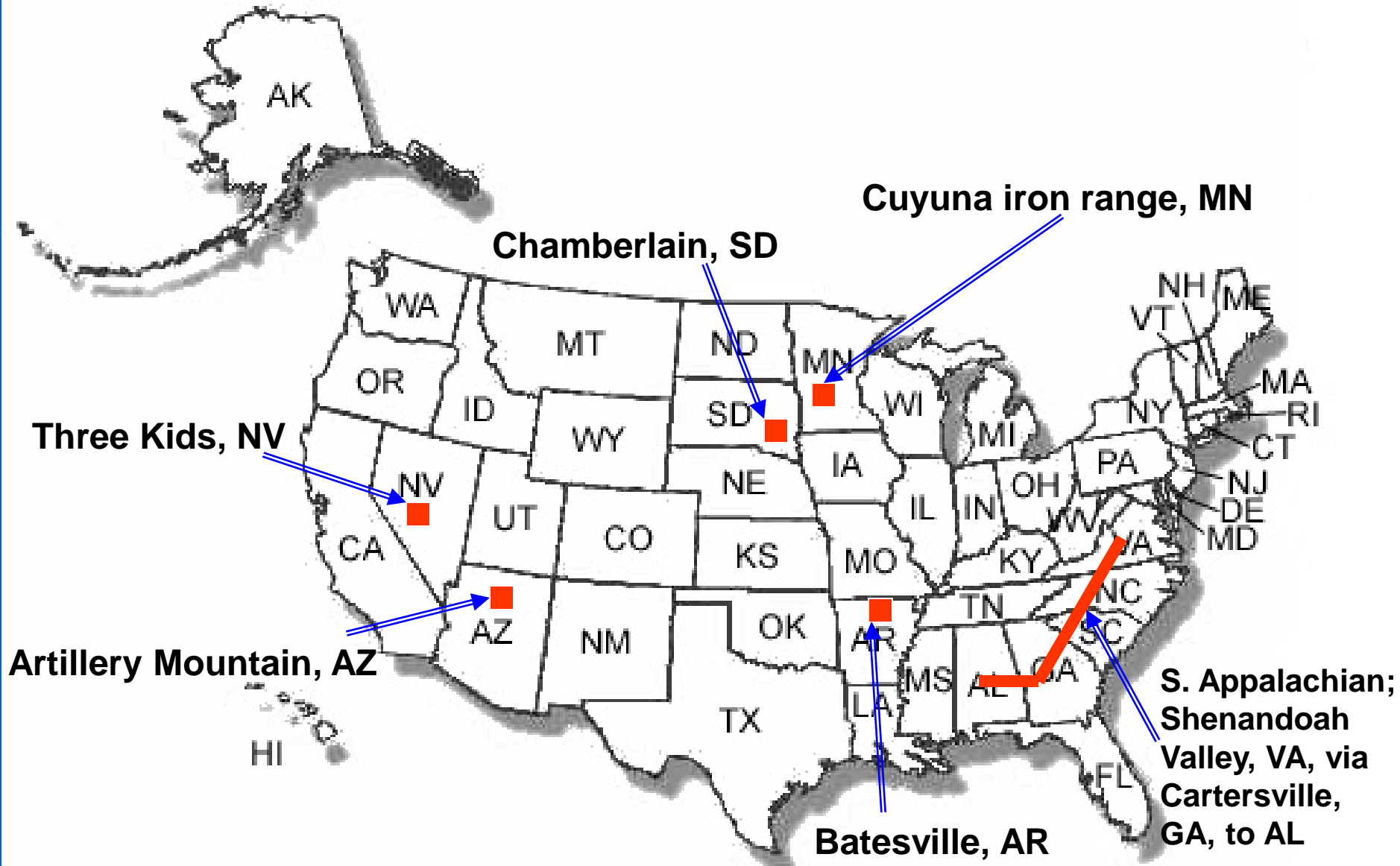
Amapa, Brazil

Kalahari, S. Africa

Groote Elyandt, Australia



Major Mn deposits in USA



Mn Minerals Production

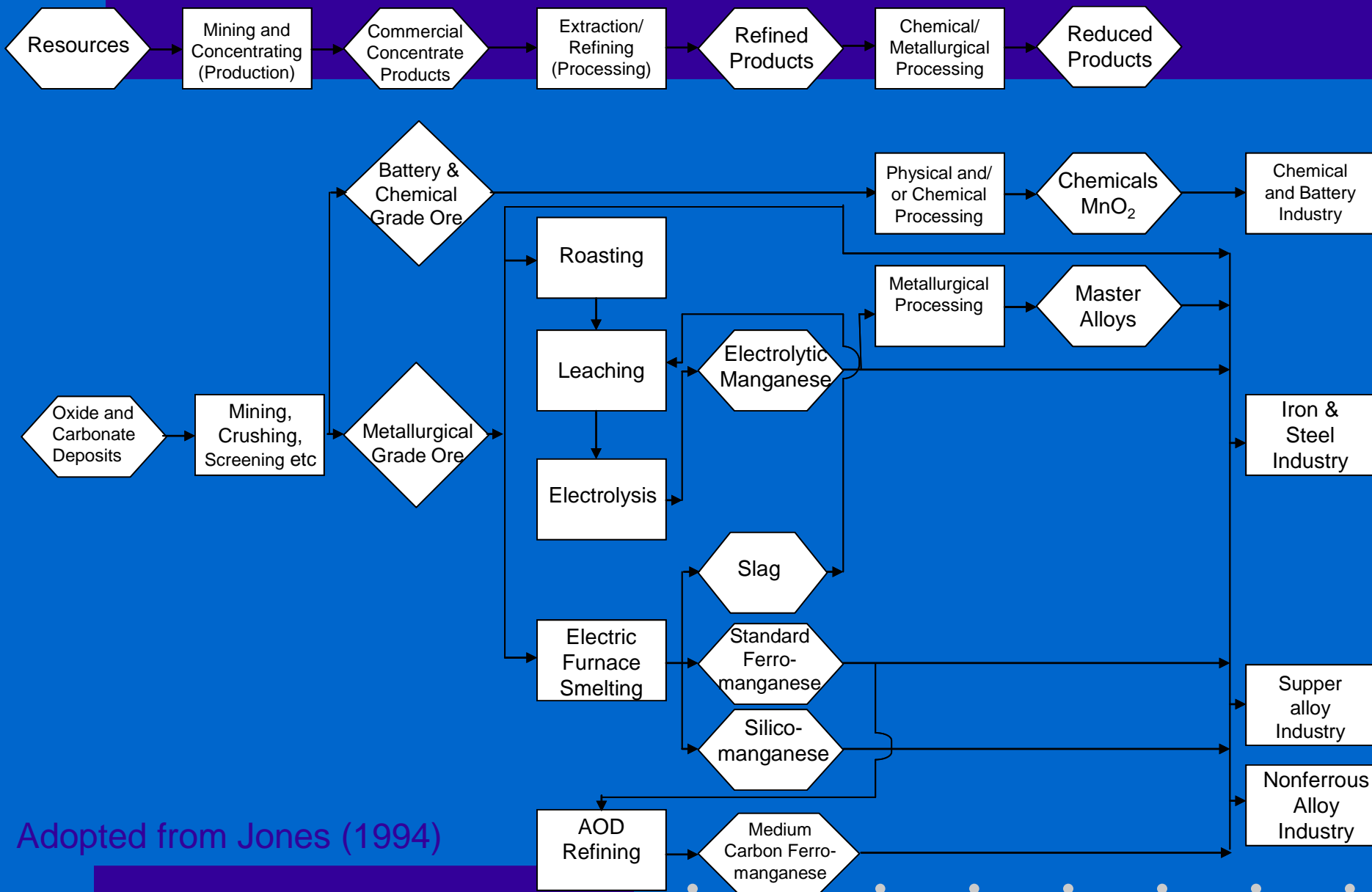
Salient Statistics—United States:¹	2007	2008	2009	2010	2011^e
Production, mine ²	—	—	—	—	—
Imports for consumption:					
Manganese ore	602	571	269	489	570
Ferromanganese	315	448	153	326	390
Silicomanganese ³	414	365	130	297	400
Exports:					
Manganese ore	29	48	15	14	1
Ferromanganese	29	23	24	19	8
Silicomanganese	3	7	19	9	10
Shipments from Government stockpile excesses: ⁴					
Manganese ore	101	9	3	—	-300
Ferromanganese	68	18	25	26	11
Consumption, reported: ⁵					
Manganese ore ⁶	351	464	422	468	470
Ferromanganese	272	304	242	292	300
Silicomanganese	92	113	94	97	100
Consumption, apparent, manganese ⁷	979	844	451	758	810
Price, average, 46% to 48% Mn metallurgical ore, dollars per metric ton unit, contained Mn:					
Cost, insurance, and freight (c.i.f.), U.S. ports ^e	3.10	12.15	7.95	9.18	9.10
CNF ⁸ China, Ryan's Notes	6.05	14.70	5.61	7.23	⁹ 6.13
Stocks, producer and consumer, yearend:					
Manganese ore ⁶	190	255	115	89	90
Ferromanganese	31	27	31	30	30
Silicomanganese	22	24	26	28	28
Net import reliance ¹⁰ as a percentage of apparent consumption	100	100	100	100	100

World Mine Production and Reserves (metal content): Reserve estimates have been revised from those previously published for Brazil (upward), Gabon (downward), and South Africa (upward), as reported by the Government of Brazil and the major manganese producers in Gabon and South Africa.

	Mine production		Reserves¹³
	<u>2010</u>	<u>2011^e</u>	
United States	—	—	—
Australia	3,100	2,400	93,000
Brazil	^e 780	1,000	110,000
China	^e 2,600	2,800	44,000
Gabon	1,420	1,500	21,000
India	^e 1,000	1,100	56,000
Mexico	175	170	4,000
South Africa	2,900	3,400	150,000
Ukraine	^e 540	340	140,000
Other countries	<u>1,340</u>	<u>1,400</u>	<u>Small</u>
World total (rounded)	13,900	14,000	630,000

World Resources: Land-based manganese resources are large but irregularly distributed; those of the United States are very low grade and have potentially high extraction costs. South Africa accounts for about 75% of the world's identified manganese resources, and Ukraine accounts for 10%.

Manganese Flow Sheet



Adopted from Jones (1994)

Uses of Manganese

- Manufacture of steel and other important alloys
 - Mn removes impurities such as sulfur and oxygen and improves rolling and forging qualities as well as strength, toughness, and durability in steel
- Depolarizer in dry cells
- Pigments, glazes, colors, paint dryers and preservatives
- As a catalyst and laboratory reagent, e.g., potassium permanganate



Uses of Manganese

- Enzymes for the metabolism of fats and proteins
- Food supplement
 - To regulate blood sugar levels and support the immune system
 - To aid bone development and reproduction
 - To provide vitamin K and the B-complex group
- Dry feeds for cattle, pigs, & poultry
 - It helps to prevent breeding complications in cattle, ensures optimum growth for pigs, and aids hatchability and shell quality in poultry
- Fertilizers and fungicides



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Nepheline syenite

Nepheline syenite

- light-colored, silica-deficient feldspathic igneous rock
- sodium and potassium feldspars
- nepheline, no quartz
- not mined in US but in Canada

Nepheline syenite—properties

- In glass, alumina from nepheline syenite improves product hardness, durability, and resistance to chemical corrosion
- in ceramics, nepheline syenite is used as a flux, melting at an early stage in the firing process and forming a glassy matrix that bonds together the other components of the system

Nepheline syenite

- alumina acts as a matrix of stabilizer, enhancing the workability of molten glass, and increasing the resistance for scratching, breaking and chemical protection
- alkali acts as a flux agent, lowering the melting temperature of the batch (no need for soda ash)

Uses

- Glass
- Ceramics
- Fillers, extenders, paint, coatings, roofing granules
- Dimension stone, aggregate, abrasive
- Alumina source
 - Russia produces most of its alumina from nepheline syenite

Table 3. Production of nepheline syenite, by country, t

Year	Russia	Canada	Norway	Turkey	South Africa*
1980	na [†]	599,699	217,000	na	na
1981	na	587,565	223,000	na	na
1982	na	552,838	224,000	na	na
1983	na	523,249	219,565	na	na
1984	na	520,640	225,731	na	na
1985	na	467,186	227,465	na	na
1986	na	467,491	218,421	na	na
1987	na	506,415	240,000	na	na
1988	na	539,835	287,000	na	na
1989	na	555,728	na	6,000	na
1990	na	na	306,000	6,000	na
1991	na	486,000	292,000	6,000	20,966
1992	1,500,000	566,000	340,000	6,000	na
1993	1,390,000	549,000	315,000	6,000	na
1994	1,500,000	602,000	279,000	18,000	98,667
1995	1,500,000	616,000	294,000	35,000	145,459
1996	1,300,000	606,000	300,000	na	137,706
1997	940,000	647,000	310,000	114,201	114,201
1998	889,000	636,000	319,835	11,500	104,000
1999	772,000	676,000	304,592	na	82,000
2000	814,000	717,000	330,000	na	na
2001	na	734,000	330,362	na	na
2002	na	724,000	330,461	na	na

Adapted from Guillet 1994; Bolger 1995; Levine 1995, 1996; Minister of Industry 1999, 2001; Levine and Wallace 2000; British Geological Survey 2002; Gurmendi 2002; Kuo 2002; Natural Resources of Canada 2003; Taylor et al. 2003; Chapman et al. 2004.

* Production from South Africa was for crushed and broken stone.

† na = not available.

Table 5. Comparison of chemical compositions of nepheline syenite, %

Oxide	Khibiny, Russia	York River (Nepheline Gneiss), Ontario	Obedjiwan, Quebec	Mount Copeland, British Columbia	Iivaara (Ijolite), Finland	Loch Borolan, Scotland	Norra Karr, Sweden	Jabal Sawda, Saudi Arabia	Jabal Abu Khuruq, Egypt
SiO ₂	54.01	41.73	54.65	56.9	46.15	48.19	56.37	50.3	63.49
TiO ₂	1.20	0.29	1.07	0.55	0.38	1.75	0.01	0.07	0.03
Al ₂ O ₃	21.05	27.48	20.91	21.0	15.7	18.52	24.95	25.8	20.56
Fe ₂ O ₃	2.60	1.84	2.38	2.6	6.59	4.51	0.31	1.39	1.2
FeO	1.80	4.52	3.79	2.6	na [*]	1.68	0.20	0.46	na
MgO	0.77	1.24	1.11	0.7	5.52	1.12	0.07	0.18	0.18
CaO	1.80	6.78	0.56	1.6	14.16	10.29	0.25	1.46	0.64
K ₂ O	5.30	3.16	7.21	6.1	2.61	8.05	5.20	4.48	5.99
Na ₂ O	9.50	11.05	6.25	7.5	7.24	3.44	11.73	9.38	7.48
MnO	0.17	trace	0.06	0.24	0.18	na	0.05	0.06	0.24
P ₂ O ₅	0.09	0.14	0.05	0.02	0.77	na	0.01	0.03	0.04
CO ₂	na	0.93	0.64	0.2	na	na	na	na	na
Loss on ignition (LOI)	1.14	0.52	1.14	0.5	0.93	3.45	0.1	5.93	na
Total	99.43	99.68	99.82	100.51	100.23	101.00	99.25	99.54	99.85

Adapted from Shand 1939; Baragar 1953; Tilley 1953; Lehtjarvi 1960; Currie 1976; Liddicoat, Ramsay, and Hedge 1985; Hosterman, Patterson, and Good 1990; Landoll, Foland, and Henderson 1994; *Industrial Minerals* 2003.

* na = not available.

Table 13. Typical glass-grade compositions of nepheline syenite, wt %

Chemical Composition	Unimin Canada A Grade	Unimin Canada B Grade	North Cape	
SiO ₂	60.2	60.1	55.9	
Al ₂ O ₃	23.5	23.4	24.2	
Fe ₂ O ₃	0.08	0.35	0.1	
MgO	trace	trace	trace	
CaO	0.3	0.3	1.3	
K ₂ O	5.1	4.9	9.0	
Na ₂ O	10.6	10.5	7.9	
P ₂ O ₅			0.1	
LOI	0.4	0.3	1.0	
Sieve Analyses, %	U.S. Sieve No.	U.S. Sieve No.	Tyler Sieve No., %	
On 25 mesh	0.0	0.0	On 28 mesh	0.0
30	0.1	0.1	32	0.1
40	14.5	14.0	53	4.9
50	48.0	46.0	48	30.0
100	86.0	84.0	65	52.0
200	98.0	97.2	200	89.0
Pan	2.0	2.8	Pan	11.0

Adapted from Minnes, Lefond, and Blair 1983; Guillet 1994.

Table 14. Chemical analyses and physical properties of products from Nephton, Ontario

Properties	MATRIX Glassy Phase Promoters (Fiberglass) 131	MATRIX Glassy Phase Promoters (Fiberglass) 134	SPECTRUM Ceramic Fluxes
SiO ₂ , wt %	60.00	59.70	60.20
Al ₂ O ₃ , wt %	23.40	23.40	23.60
Fe ₂ O ₃ , wt %	0.1	0.34	0.08
CaO, wt %	0.44	0.56	0.35
MgO, wt %	0.02	0.03	0.02
Na ₂ O, wt %	10.30	10.30	10.50
K ₂ O, wt %	5.20	5.10	4.80
LOI, %	0.51	0.61	0.42
Free-silica content	<0.1%	<0.1%	<0.1%
pH	10.1	10.1	10.1
Melting point	1,868°F/1,020°C	1,868°F/1,020°C	1,868°F/1,020°C
Bulk density, loose	83–87 lb/ft ³	83–87 lb/ft ³	38–55 lb/ft ³
Specific gravity	2.61 g/cm ³	2.61 g/cm ³	2.61 g/cm ³

Adapted from Unimin Corp.

Table 1. Major worldwide nepheline syenite mines and deposits

Mine	Company	Mining Method	Startup Date	Capacity, tpy	Comments
Khibiny, Kola, Russia	Apatit Production Association	3 open pit, 2 underground	1929	1,500,000	Apatite with by-product nepheline syenite produced
Lovozero massif, Kola, Russia	na*	na	na	na	By-product of REEs production from syenite, urtite
Kiya-Shaltyr and Goryachegorsk, Siberia	na	na	na	na	Aluminum production from urtite and ijolite
Blue Mountain, Havelock, Ontario	Unimin Corporation	Open pit	1955	700,000	Crush, magnetic separation, sizing, fine grinding
Blue Mountain, Nephton, Ontario	Unimin Corporation	Open pit	1936	Included with Havelock Mine	Crush, magnetic separation, sizing, fine grinding
North Cape, Stjernoya, Norway	North Cape Minerals AS (owned by Unimin)	Underground	1961	330,000	Nepheline syenite
Fourche Mountain, Arkansas, United States	3M Company	Open pit	1947		Roofing granules, construction aggregates
Canaan, Rio de Janeiro, Brazil	Unimin Corporation		1980	134,000	Litchfieldite
Sichuan, Shuiye, Anyang, Henan Province, China	Fineton Industrial Minerals Ltd.	Under development	1994	35,000	100,000 t of ore
Bursa Orhaneli, Turkey	Matel Hammade San ve Tic AS	Open pit	na	na	40 Mt of nepheline syenite
South Africa		Quarries	na	na	Crushed stone, nepheline syenite

Adapted from Woolley 1987; *Industrial Minerals* 2003.

*na = not available.



Figure 1. Nepheline syenite mines and deposits worldwide

Silica

- Quartz
- Citrine—yellow to brown color, similar to topaz
- Tridymite
- Cristobalite
- Coesite
- Stishovite
- Melanophlogite
- Lechatelierite
- Agate—banded, multicolored
- Flint—gray to black, opaque
- Chalcedony—fine grained chert
 - Carnelian—red to reddish brown

Silica—introduction

- SiO₂
- industrial sand and gravel
- silicon
- quartz crystals
- special silica stone products
- tripoli (microcrystalline silica)
 - rottenstone
- novacullite (whetstones, microcrystalline silica)
- spiculite



Table 2.—Common products containing 0.1% or more crystalline silica

At Work	At Home	Everywhere
(in the process of manufacturing or using the following items)	(as a consumer of the following items)	(exposure could be on the job or at home)
<p>Asphalt filler—is usually composed of quartz and stone aggregate.</p> <p>Bricks—have a high concentration of sand. Contains quartz and possibly cristobalite.</p> <p>Concrete—like asphalt filler, contains stone aggregate.</p> <p>Jeweler's rouge—contains cryptocrystalline silica.</p> <p>Jewelry and crystals—amethyst and quartz are crystalline silica.</p> <p>Mortar—contains sand.</p> <p>Municipal water filter beds—are constructed from both sand (crystalline silica) and diatomite (amorphous silica).</p> <p>Plaster—is made from gypsum but sometimes contains silica.</p> <p>Plastic in appliances—can contain clay, talc, crushed limestone, and silica as fillers.</p> <p>Rafing granules—are made from sand and aggregate.</p> <p>Wallboard—is made from gypsum.</p>	<p>Art clays and glazes—contain clay, and sometimes crystalline silica.</p> <p>Cleansers—contain pumice and feldspar as abrasives.</p> <p>Cosmetics—contain talc and clay.</p> <p>Pet litter—is composed primarily of clay.</p> <p>Talcum powder—contains talc.</p> <p>Unwashed root vegetables—(such as potatoes and carrots) are coated with soil, which has a high crystalline silica content.</p> <p>Pharmaceuticals—contain clays and talc as filler. Often the dosage of active ingredient in a medication is so minute that filler (listed as an inert ingredient) must be added to make the substance manageable to take.</p> <p>Sand—is crystalline silica. Beach sand, play sand for sandboxes, and the sand used on golf courses are no different than industrial sand used for construction, in sandblasting, or on icy roads. All are largely crystalline silica.</p>	<p>Caulk and putty—contain clay, which can have a low to moderate crystalline silica content, as a filler.</p> <p>Dust—(whether household or industrial) contains crystalline silica.</p> <p>Fill dirt and topsoil—contain sand. Because the crystalline silica content of common soil is so high, agricultural workers represent the occupational group most at risk for exposure to respirable crystalline silica.</p> <p>Foam in furniture and on rug backings—contain talc and silica.</p> <p>Paint—contains clay, talc, sand, and diatomite.</p> <p>Paper and paper dust contain kaolin and clay.</p>

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Industrial sand and gravel—introduction

- Silica
- silica sand
- quartz sand
- sand and gravel with a high SiO₂ content

Industrial sand and gravel—uses

- glassmaking sand, 38%
- foundry sand, 22% (molds, cores, castings)
- abrasive sand, 5%
- hydraulic fracturing sand, 5%
- 30% for other uses (flux)

not more than 0.6% iron oxide

TABLE 1
SALIENT U.S. SILICA STATISTICS 1/

		1997	1998	1999	2000	2001
Industrial sand and gravel: 2/						
Sold or used:						
Sand:						
Quantity	thousand metric tons	26,300	26,400	26,900	26,800	26,900
Value	thousands	\$485,000	\$491,000	\$510,000	\$532,000	\$559,000
Gravel:						
Quantity	thousand metric tons	2,170	1,790	1,940	1,660	1,060
Value	thousands	\$26,300	\$22,200	\$28,400	\$24,400	\$17,600
Total:						
Quantity	thousand metric tons	28,500	28,200	28,900	28,400	27,900
Value	thousands	\$511,000	\$513,000	\$538,000	\$556,000	\$576,000
Exports:						
Quantity	thousand metric tons	980	2,400	1,670	1,660	1,540
Value	thousands	\$134,000	\$148,000	\$133,000	\$179,000	\$163,000
Imports for consumption:						
Quantity	thousand metric tons	39	44	211	247	172
Value	thousands	\$3,200	\$2,750	\$5,590	\$11,800	\$11,000
Processed tripoli: 3/						
Quantity	metric tons	81,300	79,600	84,900	72,000	60,500
Value	thousands	\$16,400	\$16,900	\$20,200	\$15,900 ^{e/}	\$15,000
Special silica stone:						
Crude production:						
Quantity	metric tons	843	649	697	553	705
Value	thousands	\$224	\$184	\$183	\$158	\$234
Sold or used:						
Quantity	metric tons	445	438	475	312	393
Value	thousands	\$2,560	\$3,440	\$3,060	\$4,610	\$4,040
Electronic and optical-grade quartz crystals, production:						
Mine	thousand kilograms	450	--	--	--	--
Cultured	do.	355	185	192	189	W

^{e/} Estimated. W Withheld to avoid disclosing company proprietary data. -- Zero.

1/ Data are rounded to no more than three significant digits; may not add to totals shown.

2/ Excludes Puerto Rico.

3/ Includes amorphous silica and Pennsylvania rottenstone.

Industrial sand and gravel—uses

- Glassmaking (high specifications, no Fe)
- foundry (98% SiO₂, low CaO, MgO, grain size and shape)
- abrasive, blasting sand (clean metal, concrete' angular shape)
- hydraulic fracturing (frac) applications (well rounded)
- ceramics
- chemicals
- ground silica (fillers, extenders; bright, reflective)
- filtration (pure)
- roofing granules
- flux
- optical fiber

Industrial sand and gravel—regions

TABLE 2
INDUSTRIAL SAND AND GRAVEL SOLD OR USED IN THE UNITED STATES, BY GEOGRAPHIC REGION 1/

Geographic region	2000				2001			
	Quantity (thousand metric tons)	Percentage of total	Value (thousands)	Percentage of total	Quantity (thousand metric tons)	Percentage of total	Value (thousands)	Percentage of total
Northeast:								
New England	104	(2/)	W	W	138	(2/)	W	W
Middle Atlantic	2,400	8	\$51,500	9	2,160	8	\$49,600	9
Midwest:								
East north-central	10,100	35	170,000	31	9,960	36	170,000	29
West north-central	1,420	5	28,700	5	1,480	5	31,200	5
South:								
South Atlantic	4,270	15	92,400	17	4,090	15	86,300	15
East south-central	2,260	8	43,100	8	2,240	8	43,200	8
West south-central	4,440	16	96,400	17	4,330	16	118,000	20
West:								
Mountain	1,360	5	22,600	4	1,380	5	24,100	4
Pacific	2,090	7	51,300	9	2,140	8	54,600	9
Total	28,400	100	556,000	100	27,900	100	576,000	100

W Withheld to avoid disclosing company proprietary data; included with "Middle Atlantic."

1/ Data are rounded to no more than three significant digits; may not add to totals shown.

2/ Less than 1/2 unit.

Industrial sand and gravel—regions

FIGURE 1
PRODUCTION OF INDUSTRIAL SAND AND GRAVEL IN THE UNITED STATES IN 2001, BY GEOGRAPHIC DIVISION

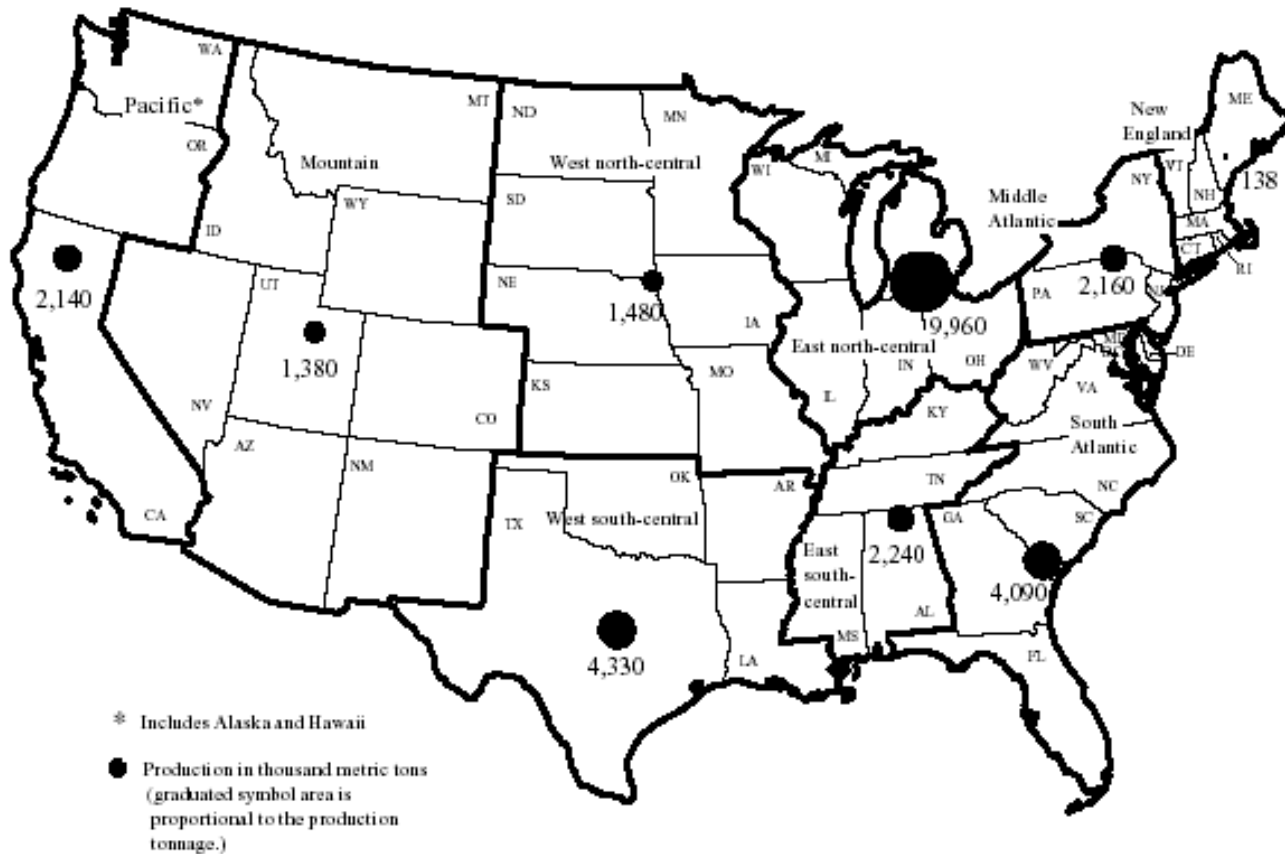


TABLE 6
INDUSTRIAL SAND AND GRAVEL SOLD OR USED BY U.S. PRODUCERS IN 2001, BY MAJOR END USE 1/

Major use	Northeast			Midwest			South		
	Quantity (thousand metric tons)	Value (thousand dollars)	Value 3/ (dollars per metric ton)	Quantity (thousand metric tons)	Value (thousand dollars)	Value 3/ (dollars per metric ton)	Quantity (thousand metric tons)	Value (thousand dollars)	Value 3/ (dollars per metric ton)
Sand:									
Glassmaking:									
Containers	W	W	18.70	1,200	13,800	11.47	1,570	25,100	15.99
Flat (plate and window)	W	W	17.14	1,290	14,000	10.92	1,730	28,100	16.21
Specialty	W	W	26.23	W	W	16.60	311	7,080	22.77
Fiberglass (unground)	--	--	--	397	5,520	13.88	W	W	16.18
Fiberglass (ground)	--	--	--	W	W	46.55	W	W	45.96
Foundry:									
Molding and core	W	W	18.75	4,850	65,900	13.58	627	10,600	16.93
Molding and core (ground)	--	--	--	W	W	80.66	W	W	97.78
Refractory	W	W	27.86	W	W	23.74	W	W	34.36
Metallurgical:									
Silicon carbide	--	--	--	W	W	18.91	--	--	--
Flux for metal smelting	--	--	--	--	--	--	W	W	5.38
Abrasives:									
Blasting	36	2,800	78.51	205	6,080	29.61	1,070	30,300	28.26
Scouring cleansers (ground)	W	W	63.80	W	W	10.92	W	W	116.59
Sawing and sanding	W	W	22.33	--	--	--	--	--	--
Chemicals (ground and unground)	W	W	20.60	W	W	13.46	315	8,920	28.31
Fillers (ground), rubber, paints, putty, etc.	W	W	13.43	146	10,200	69.47	W	W	108.77
Whole grain fillers/building products	221	6,710	30.29	515	12,700	24.56	1,120	21,100	18.95
Ceramic (ground), pottery, brick, tile, etc.	W	W	56.86	W	W	74.05	116	5,680	48.90
Filtration:									
Water (municipal, county, local, etc.)	34	1,430	41.77	73	3,180	43.71	186	5,410	29.06
Swimming pool, other	31	1,330	43.13	W	W	79.48	47	686	14.66
Petroleum industry:									
Hydraulic fracturing	--	--	--	1,030	33,900	32.98	W	W	54.97
Well packing and cementing	--	--	--	W	W	730.40	W	W	65.77
Recreational:									
Golf course (greens and traps)	W	W	16.35	254	3,620	14.24	415	4,430	10.65
Baseball, volleyball, play sand, beaches	72	1,260	17.64	W	W	34.98	W	W	10.29
Traction (engine)	33	603	18.10	79	921	11.64	47	686	14.66
Roofing granules and fillers	W	W	24.12	W	W	16.22	129	2,520	19.58
Other (ground silica)	W	W	49.10	130	7,510	57.71	442	27,000	61.15
Other (whole grain)	1,870	35,400	19.05	1,160	22,100	19.04	1,840	57,200	29.15
Total or average	2,290	49,600	21.61	11,300	199,000	17.60	9,970	235,000	23.57

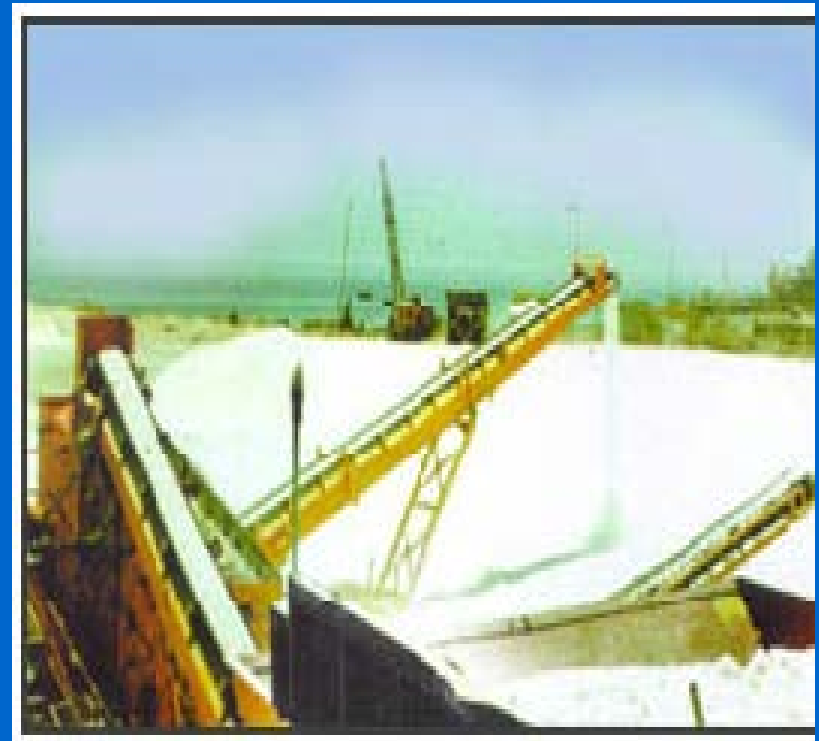
See footnotes at end of table.

Industrial sand and gravel—geology

- Sedimentary, especially where multiple cycles of erosion and deposition has upgraded the deposits
 - What geologic environments are we looking at?

Silica sand—geology

- White Maddi sand is used in foundries, filters, and glass products, Gabal El Kahshab near Maadi, Cairo



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Industrial sand and gravel—substitutions

- For glass, foundry, molding
 - Zircon
 - olivine
 - staurolite
 - chromite sands

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Silicon—introduction

- Silicon metal and alloys
- Ferrosilicon

Silicon—uses

- ferrous foundry
- steel industries
- aluminum and aluminum alloys
- chemical industry
- semiconductor industry, which manufactures chips for computers from high-purity silicon

Silicon—substitutions

- ferrosilicon
 - aluminum
 - silicon carbide
 - silicomanganese
- semiconductors and infrared
 - gallium arsenide
 - germanium

Silicon—production

Salient Statistics—United States:	2007	2008	2009	2010	2011^e
Production:					
Ferrosilicon, all grades ¹	155	180	139	176	W
Silicon metal ²	W	W	W	W	W
Total	W	W	W	W	350
Imports for consumption:					
Ferrosilicon, all grades ¹	208	190	70	157	150
Silicon metal	147	168	113	171	200
Exports:					
Ferrosilicon, all grades ¹	7	10	9	15	20
Silicon metal	28	35	38	65	82
Consumption, apparent:					
Ferrosilicon, all grades ¹	359	352	207	312	W
Silicon metal ²	W	W	W	W	W
Total	W	W	W	W	600
Price, ³ average, cents per pound Si:					
Ferrosilicon, 50% Si	74.0	116	76.9	109	110
Ferrosilicon, 75% Si	65.6	109	68.9	97.2	100
Silicon metal ²	113	162	116	140	150
Stocks, producer, yearend:					
Ferrosilicon, all grades ¹	14	21	14	20	W
Silicon metal ²	W	W	W	W	W
Total	W	W	W	W	23
Net import reliance ⁴ as a percentage of apparent consumption:					
Ferrosilicon, all grades ¹	58	49	33	44	<50
Silicon metal ²	<50	<50	<50	<50	<50
Total	W	W	W	W	42

Recycling: Insignificant.

World Production and Reserves:

	Production ^{e, 5}	
	<u>2010</u>	<u>2011</u>
United States	7176	350
Brazil	224	230
Canada	52	52
China	4,920	5,400
France	127	140
Iceland	74	75
India ⁷	66	68
Norway	303	320
Russia	643	670
South Africa	137	130
Ukraine ⁷	127	100
Venezuela ⁷	50	62
Other countries	<u>394</u>	<u>400</u>
World total (rounded)	7,290	8,000

Reserves⁶

The reserves in most major producing countries are ample in relation to demand. Quantitative estimates are not available.

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Silicon—production

- Norway, 27%
- South Africa, 15%
- Russia, 11%
- Canada, 10%

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Quartz crystal

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Quartz crystal—introduction

- Hardness 7
- any color
- common mineral
- cultured quartz crystals became important in 1971, no natural production

Quartz crystal—properties

- Piezoelectric effect
- when compressed or bent, it generates a charge or voltage on its surface
- if a voltage is applied, quartz will bend or change its shape very slightly
- hardness
- high electrical resistance
- dimensional stability

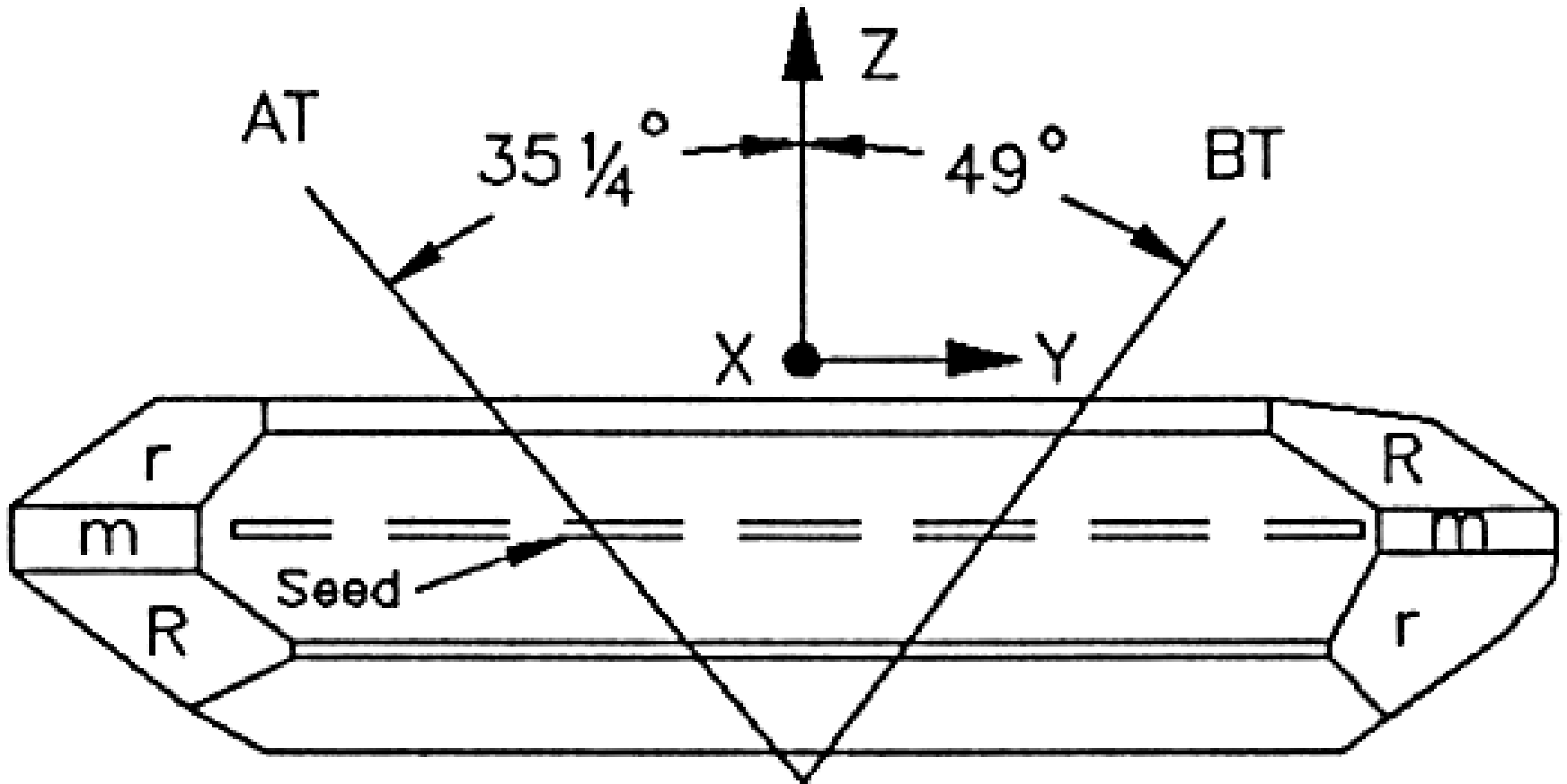
Growing quartz crystal

- Process in Germany 50 years ago
- grown in pressure vessels containing quartz dissolved in an aqueous alkaline solution at temperatures of 375 degrees centigrade and pressures of 800 to 2000 atmospheres
- Seed crystals are placed near the top of the container
- nutrient in the form of broken chunks of natural Brazilian quartz (lascas) as a nutrient are placed on the bottom
- Convection currents move dissolved material from the bottom of the chamber to the cooler upper section where it deposits on the seed crystals



<http://www.itme.edu.pl/z18/syn...>

Figure 3: Cultured Quartz Crystal



Quartz crystal—uses

- single-crystal silica
- Electronic applications
- optical applications
- filters, frequency controls, and timers in electronic circuits
- carvings
- gem stone

Quartz crystal—geology

- Pegmatites
- in Arkansas veins filled cavities or fractures in the Crystal Mountain and Blakely Sandstones
 - 5 feet long and weighing over 500 pounds and clusters up to 15 feet long by 10 feet wide, weighing over 10 tons
 - end of the Ouachita Mountain orogenic cycle in Late Pennsylvanian to Early Permian (Ar/Ar)

Quartz—production

TABLE 11
SALIENT U.S. ELECTRONIC- AND OPTICAL-GRADE QUARTZ CRYSTAL STATISTICS 1/

(Thousand kilograms and thousand dollars)

	1997	1998	1999	2000	2001
Production:					
Mine	450	--	--	--	--
Cultured e/	355	185	192	189	W
Exports (cultured): 2/					
Quantity	74	63	90	74	38
Value	31,100	24,300	25,400	22,800	10,600
Imports (cultured): 2/					
Quantity	63	47	26	31	14
Value	11,700	12,200	11,000	14,300	8,390
Consumption, apparent e/	343	169	128	146	W

e/ Estimated. W Withheld to avoid disclosing company proprietary data. -- Zero.

1/ Data are rounded to no more than three significant digits.

2/ Excludes mounted piezoelectric crystals.

Special silica stone products—introduction

- abrasive tools
 - deburring media
 - grinding pebbles
 - grindstones, hones,
 - oilstones
 - stone files
 - tube-mill liners
 - whetstones
- Fillers
- extenders
- flux

Special silica stone products—introduction

- Sandstone
- quartzite
- vein quartz
- silica pebble
- novaculite
- microcrystalline quartz
- specularite
- tripoli
- tripolite or diatomaceous earth
- amorphous silica

Novaculite

- Sedimentary microcrystalline quartz
- homogeneous
- more compact than porous tripoli
- whetstones
- dense, hard, white to grayish-black in color, translucent on thin edges, and has a dull to waxy luster
- resistant to erosion, it forms prominent ridges
- Dev to Miss Novaculite Formation in Ark
 - 250-900 ft thick



Rottenstone

- Common variety of tripoli
- Penn--weathering of siliceous shale



Spiculite

- Siliceous sponge spicules
- replacement of spicule-bearing limestone
- Texas



Tripoli

- 1 to 10 micrometers
- 98% to 99% silica, minor Al and Fe
- white to cream
- brown
- red
- yellow
- abrasive
- diatomaceous earth (different origin)

Tripoli—geology

- alteration of chert, chalcedony, or novaculite, or leaching of highly siliceous limestones
- Paleozoic chert bearing limestones in Arkansas and Oklahoma, Illinois
 - NE Ar cherty limestones of the Boone Formation (Mississippian)
 - Ouachita Mountains leaching of a limy phase within the Upper Division of the Arkansas Novaculite
- Arkansas tripoli is $>99\%$ SiO_2

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Special silica stone products—source

- Arkansas
- Wisconsin

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Special silica stone products—uses

- Craft
- household
- industrial
- leisure uses

Special silica stone products

TABLE 10
U.S. PRODUCERS OF SPECIAL SILICA STONE PRODUCTS IN 2001

Company and location	Type of operation	Product
B&C Abrasives, Inc., Hot Springs, AR	Stone cutting and finishing	Whetstones and oilstones.
Blue Mountain Whetstone Co., Hot Springs, AR	do.	Do.
Buffalo Stone Corp., Hot Springs, AR	Tumbling and sizing novaculite	Metal finishing media deburring media.
Dan's Whetstone Co., Inc., Hot Springs, AR	Stone cutting and finishing	Whetstones and oilstones.
Do.	Quarry	Crude novaculite.
Hall's Arkansas Oilstones, Inc., Pearcy, AR	Stone cutting and finishing	Whetstones and oilstones.
The Kraemer Co., Baraboo, WI	Crushing and sizing	Deburring media.
Do.	Quarry	Crude silica stone.
Norton Company Oilstones:		
Hot Springs, AR	do.	Do.
Littleton, NH	Stone cutting and finishing	Whetstones and oilstones.
Smith Abrasives, Inc., Hot Springs, AR	do.	Do.
Do.	Quarry	Crude novaculite.
Taylor Made Crafts Inc.:		
Hot Springs, AR	Stone cutting and finishing	Whetstones and oilstones.
Pearcy, AR	Quarry	Crude novaculite.

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- # Environmental regulations of quartz

- regulation of crystalline silica
 - hours workers exposure
 - water well monitoring
 - noise and dust control
 - water discharge
 - archaeological surveys
 - carcinogen

Production—niobium

Salient Statistics—United States:

	<u>2007</u>	<u>2008</u>	<u>2009</u>	<u>2010</u>	<u>2011^e</u>
Production:					
Mine	—	—	—	—	—
Secondary	NA	NA	NA	NA	NA
Imports for consumption ^{e, 1}	10,120	9,230	4,400	8,500	9,200
Exports ^{e, 1}	1,100	781	195	281	430
Government stockpile releases ^{e, 2}	—	—	—	—	—
Consumption: ^e					
Apparent	9,020	8,450	4,210	8,070	8,800
Reported ³	6,510	5,380	4,350	5,590	4,400
Unit value, ferroniobium, dollars per metric ton ⁴	21,918	34,398	37,298	37,781	41,000
Net import reliance ⁵ as a percentage of apparent consumption	100	100	100	100	100

World Mine Production and Reserves: Canada's reserves were changed to proven plus probable reserves from proven reserves; data were updated (for the Niobec Mine) and another property added (Thor Lake), based on company reports.

	<u>Mine production</u>		<u>Reserves⁸</u>
	<u>2010</u>	<u>2011^e</u>	
United States	—	—	—
Brazil	58,000	58,000	2,900,000
Canada	4,420	4,400	200,000
Other countries	520	600	NA
World total (rounded)	62,900	63,000	3,000,000

Production—tantalum

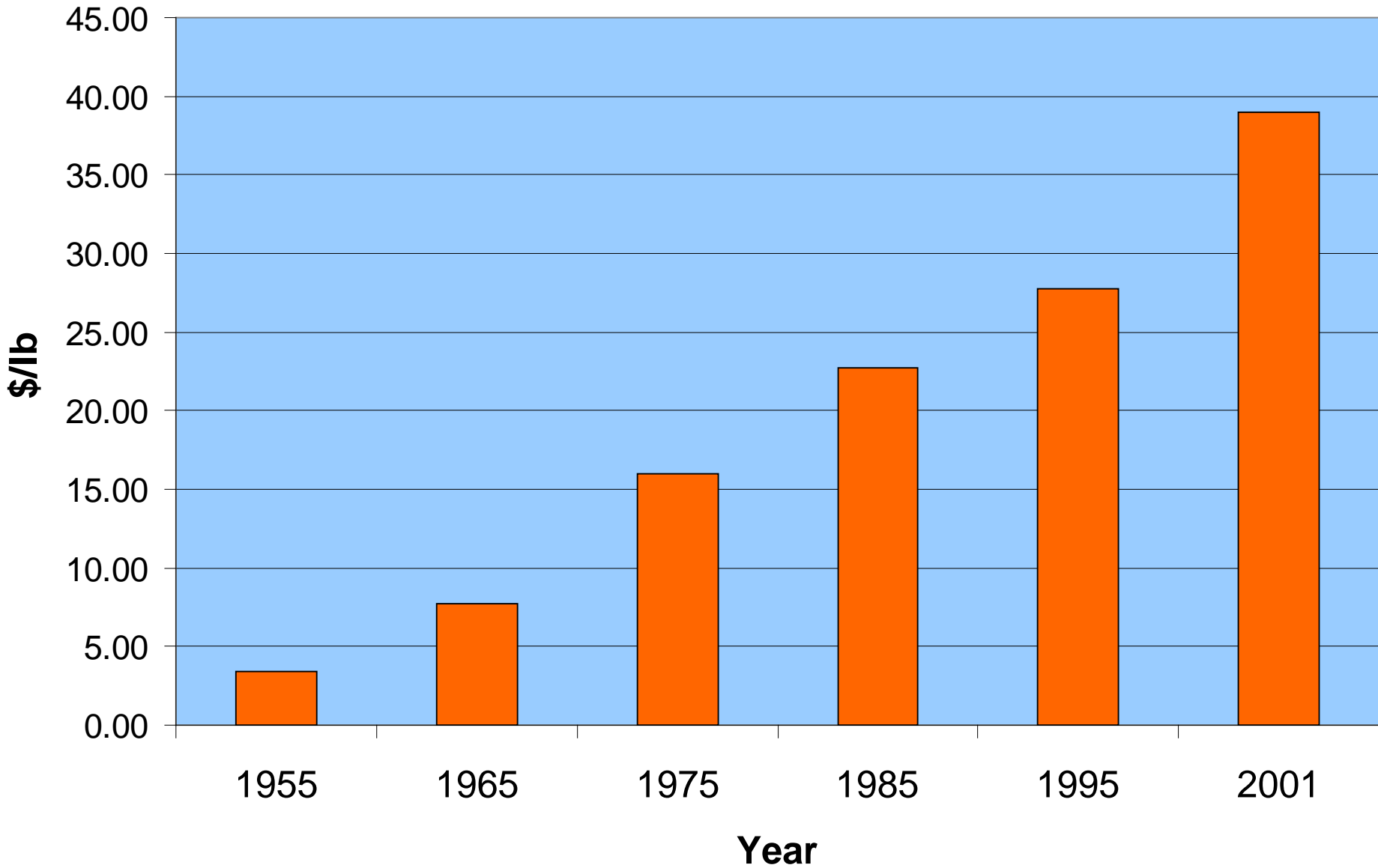
Salient Statistics—United States:

	<u>2007</u>	<u>2008</u>	<u>2009</u>	<u>2010</u>	<u>2011^e</u>
Production:					
Mine	—	—	—	—	—
Secondary	NA	NA	NA	NA	NA
Imports for consumption ^{e, 1}	1,160	1,290	798	1,600	1,700
Exports ^{e, 1}	511	662	326	438	540
Government stockpile releases ^{e, 2}	—	—	—	—	—
Consumption, apparent	644	629	473	1,160	1,200
Price, tantalite, dollars per pound of Ta ₂ O ₅ content ³	37	44	40	54	130
Net import reliance ⁴ as a percentage of apparent consumption	100	100	100	100	100

World Mine Production and Reserves: Reserves for Australia were raised to agree with the Government of Australia's "Accessible Economic Demonstrated Resources."

	<u>Mine production⁸</u>		<u>Reserves⁹</u>
	<u>2010</u>	<u>2011^e</u>	
United States	—	—	—
Australia	—	80	51,000
Brazil	180	180	65,000
Canada	—	25	NA
Mozambique	120	120	3,200
Rwanda	110	110	NA
Other countries ¹⁰	<u>271</u>	<u>270</u>	<u>NA</u>
World total (rounded)	681	790	120,000

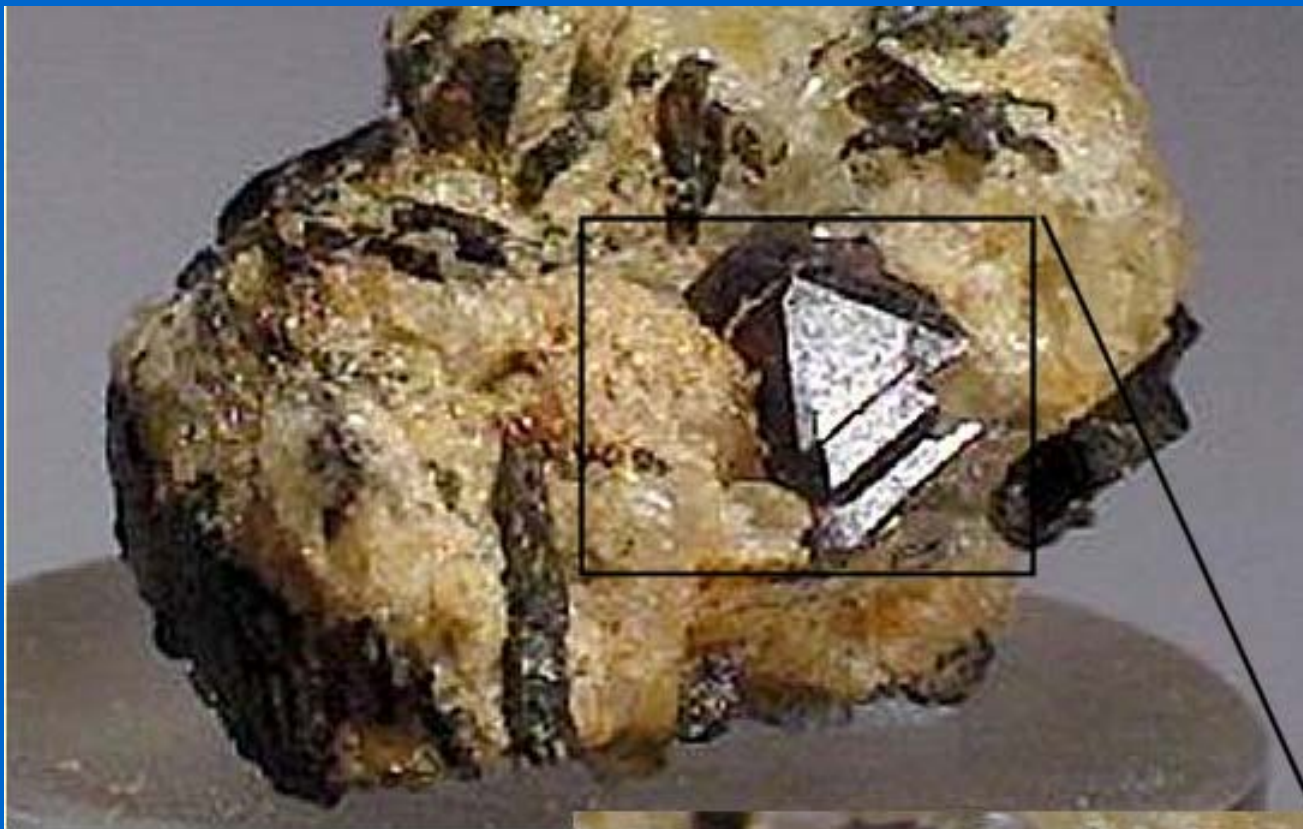
Tantalum Price vs. Time



Niobium—geology

<http://www.tanb.org/niobium1.html>

- pyrochlore $[(Ca,Na)_2 Nb_2(O,OH,F)^7]$ in carbonatite and alkaline igneous deposits
- pegmatites (Columbite and tantalite)
- alluvial deposits
- largest deposit in Araxá, Brazil, owned by Companhia Brasileira de Metalurgia e Mineração (CBMM) (460 million tons of 3.0% Nb_2O_5 , or 500 yrs reserves)
- Niobec mine in Quebec
- tin slags produced from the smelting of cassiterite ores



Closeup of
rectangular area.



Lauzon
Farm, Oka,
Quebec,
Canada. 3.9
x 2.9 cm.
<http://www.webmi>



Companhia Brasileira de Metalurgia e
Mineração (CBMM), open pit mine for Nb,
Minas Gerais, Brazil

http://www.us.cbmm.com.br/english/sources/mine/operat/f_operat.htm

Zircon—introduction

- ZrSiO_4
- baddeleyite ZrO_2
- highly resistant to weathering
- high specific gravity 4.6-4.7
- other potential minerals
 - Eudialyte
 - gittinsite

Zircon—introduction

- Zr resistant to corrosion by acids and other chemicals
- alloyed with Nb it becomes superconductive (conduct electricity with very little loss of energy to electric resistance)
- does not absorb neutrons

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Hafnium—introduction

- Hf
- in zircon and baddeleyite

Zircon—uses

- zircon ceramics
- opacifiers
- refractories
- foundry applications
- abrasives
- chemicals
- metal alloys
- welding rod
- coatings
- sandblasting



Hafnium—uses

- addition in superalloys



Production

Salient Statistics—United States:	2007	2008	2009	2010	2011^e
Production, zircon (ZrO ₂ content)	W	W	W	W	W
Imports:					
Zirconium, ores and concentrates (ZrO ₂ content)	13,000	22,300	9,370	14,900	13,600
Zirconium, unwrought, powder, and waste and scrap	299	318	451	726	648
Zirconium, wrought	485	715	526	435	359
Zirconium oxide ¹	3,740	5,060	2,810	2,920	2,850
Hafnium, unwrought, powder, and waste and scrap	4	12	5	8	12
Exports:					
Zirconium ores and concentrates (ZrO ₂ content)	43,000	27,400	25,700	30,800	15,500
Zirconium, unwrought, powder, and waste and scrap	328	591	223	519	488
Zirconium, wrought	1,830	2,080	2,080	1,540	1,180
Zirconium oxide ¹	2,400	2,970	3,050	5,630	6,250
Consumption, zirconium ores and concentrates, apparent (ZrO ₂ content)	W	W	W	W	W
Prices:					
Zircon, dollars per metric ton (gross weight):					
Domestic ²	763	788	830	860	2,500
Imported, f.o.b. ³	872	773	850	1,155	2,100
Zirconium, unwrought, import, France, dollars per kilogram ⁴	29	41	51	74	64
Hafnium, unwrought, import, France, dollars per kilogram ⁴	246	225	472	453	562
Net import reliance ⁵ as a percentage of apparent consumption:					
Zirconium	E	E	E	E	E
Hafnium	NA	NA	NA	NA	NA

**Zirconium mine production
(thousand metric tons)**

**Zirconium reserves⁶
(thousand metric tons, ZrO₂)**

	<u>2010</u>	<u>2011^e</u>	
United States	W	W	500
Australia	518	720	21,000
Brazil	18	18	2,200
China	140	100	500
India	38	38	3,400
Indonesia	50	50	NA
Mozambique	37	40	1,200
South Africa	400	380	14,000
Ukraine	30	35	4,000
Other countries	14	32	<u>5,000</u>
World total (rounded)	⁷ <u>1,250</u>	⁷ <u>1,410</u>	<u>52,000</u>

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Zircon—geology

- Beach sands in Florida, Virginia and South Carolina (with Ti)