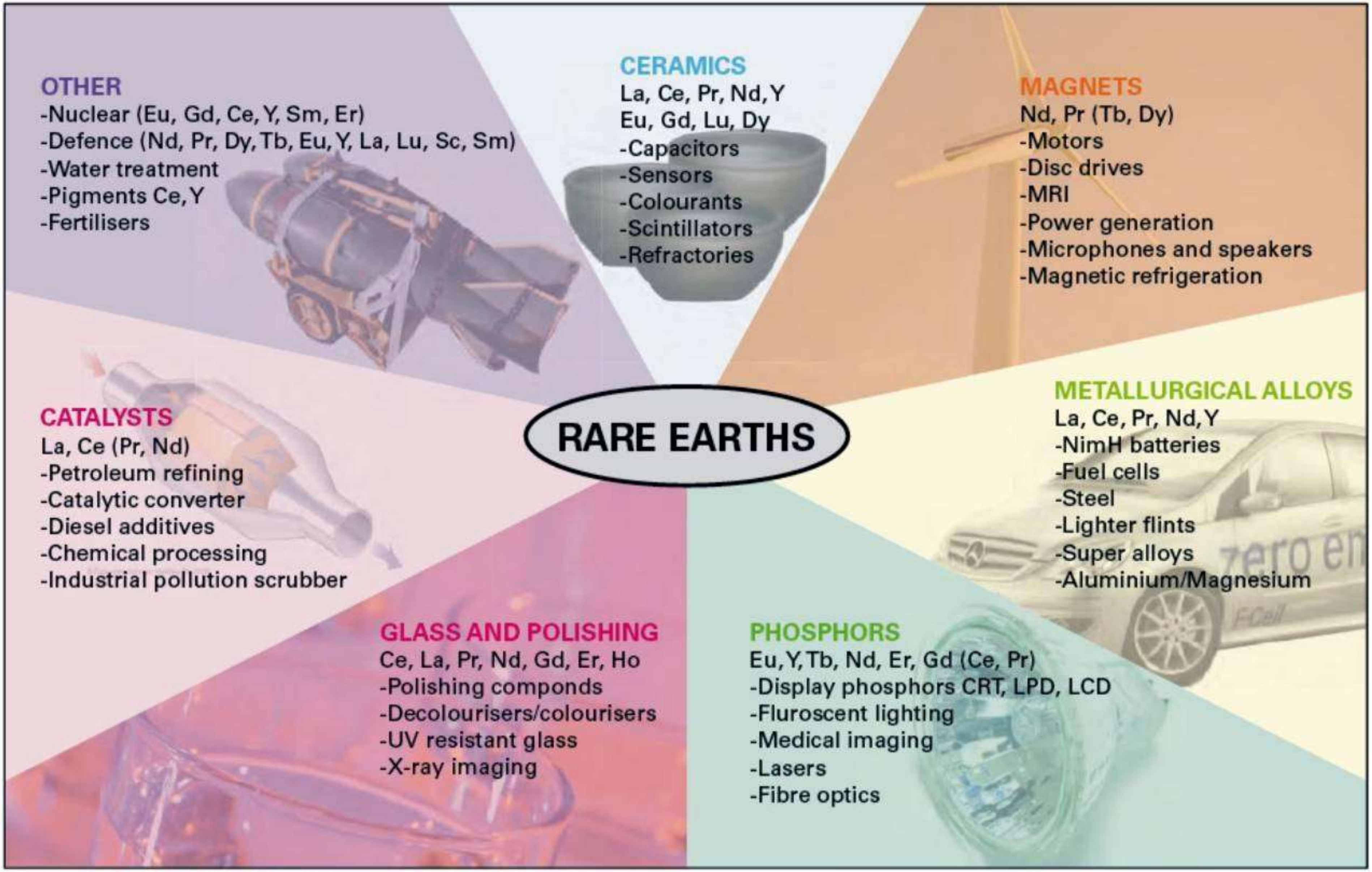


RARE EARTHS

OTHER
- Nuclear (Eu, Gd, Ce, Y, Sm, Er)
- Defence (Nd, Pr, Dy, Tb, Eu, Y, La, Lu, Sc, Sm)
- Water treatment
- Pigments Ce, Y
- Fertilisers

CERAMICS
La, Ce, Pr, Nd, Y
Eu, Gd, Lu, Dy
- Capacitors
- Sensors
- Colourants
- Scintillators
- Refractories

MAGNETS
Nd, Pr (Tb, Dy)
- Motors
- Disc drives
- MRI
- Power generation
- Microphones and speakers
- Magnetic refrigeration

CATALYSTS
La, Ce (Pr, Nd)
- Petroleum refining
- Catalytic converter
- Diesel additives
- Chemical processing
- Industrial pollution scrubber

METALLURGICAL ALLOYS
La, Ce, Pr, Nd, Y
- NimH batteries
- Fuel cells
- Steel
- Lighter flints
- Super alloys
- Aluminium/Magnesium

GLASS AND POLISHING
Ce, La, Pr, Nd, Gd, Er, Ho
- Polishing componds
- Decolourisers/colourisers
- UV resistant glass
- X-ray imaging

PHOSPHORS
Eu, Y, Tb, Nd, Er, Gd (Ce, Pr)
- Display phosphors CRT, LPD, LCD
- Fluroscent lighting
- Medical imaging
- Lasers
- Fibre optics

REE criticality

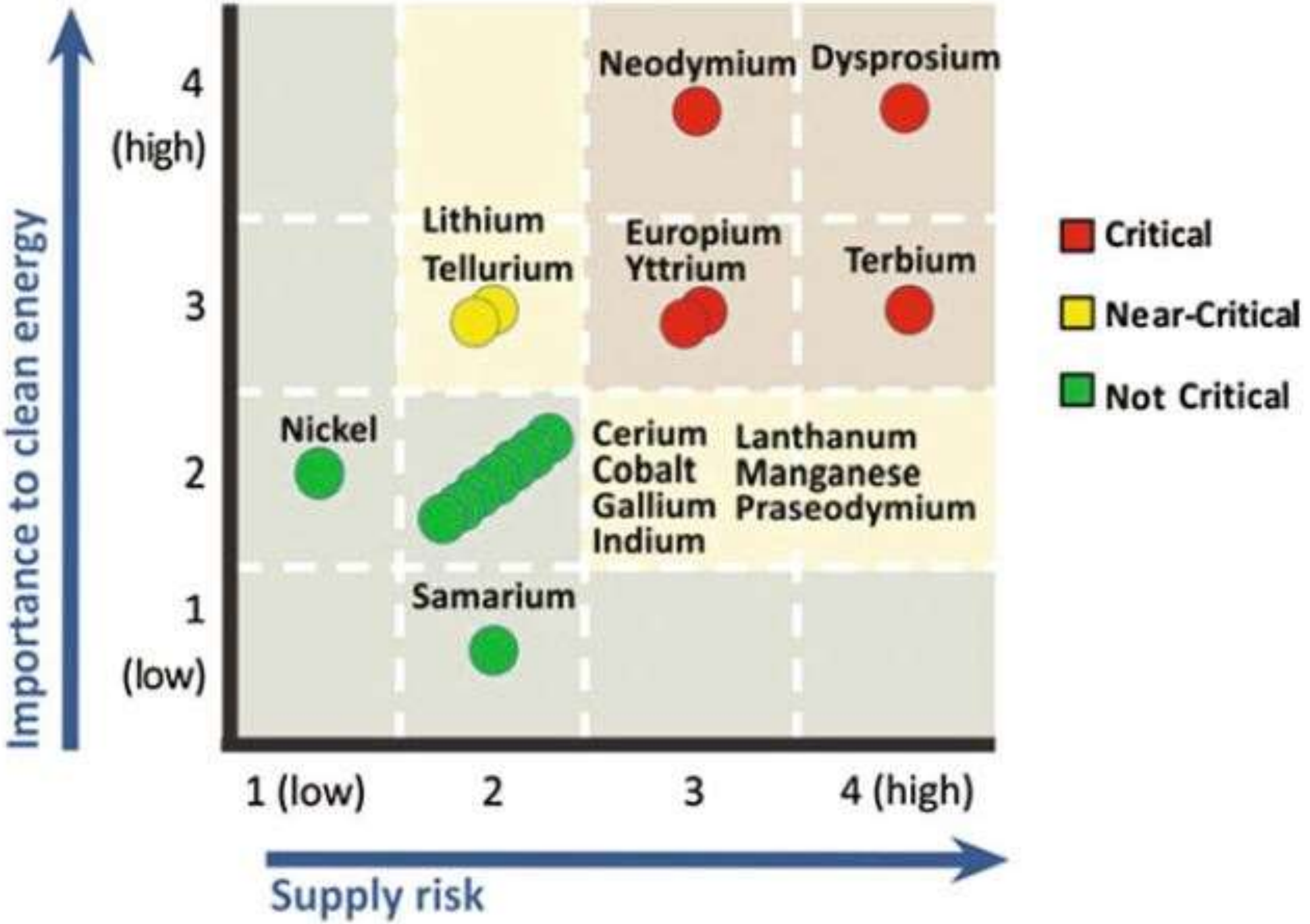


Fig. 7.2 DOE medium-term (2015–2025) criticality matrix, showing the five most critical rare earth elements (Y, Nd, Eu, Tb, Dy), and the non-critical ones (Ce, Pr, Sm). Reproduced with permission of the U.S. Department of Energy (2011)

REE

REE Element	Symbol	Atomic number	Atomic weight	Density (g/cm³)	Melting point (°C)	Clarke (ppm)
Scandium	Sc	21	44.95	2.989	1541	14
Yttrium	Y	39	88.90	4.469	1522	21
Lanthanum	La	57	138.90	6.146	918	30
Cerium	Ce	58	140.11	8.160	798	63
Praseodymium	Pr	59	140.90	6.773	931	7.1
Neodymium	Nd	60	144.24	7.008	1021	27
Promethium	Pm	61	145.00	7.264	1042	n.a.
Samarium	Sm	62	150.36	7.520	1074	4.7
Europium	Eu	63	151.96	5.244	822	1.0
Gadolinium	Gd	64	157.25	7.901	1313	4.0
Terbium	Tb	65	158.92	8.230	1356	0.7
Dysprosium	Dy	66	162.50	8.551	1412	3.9
Holmium	Ho	67	164.93	8.795	1474	0.83
Erbium	Er	68	167.26	9.066	1529	2.3
Thulium	Tm	69	168.93	9.321	1545	0.30
Ytterbium	Yb	70	173.04	6.966	819	1.96
Lutetium	Lu	71	174.97	9.841	1663	0.31

REE – crustal abundance

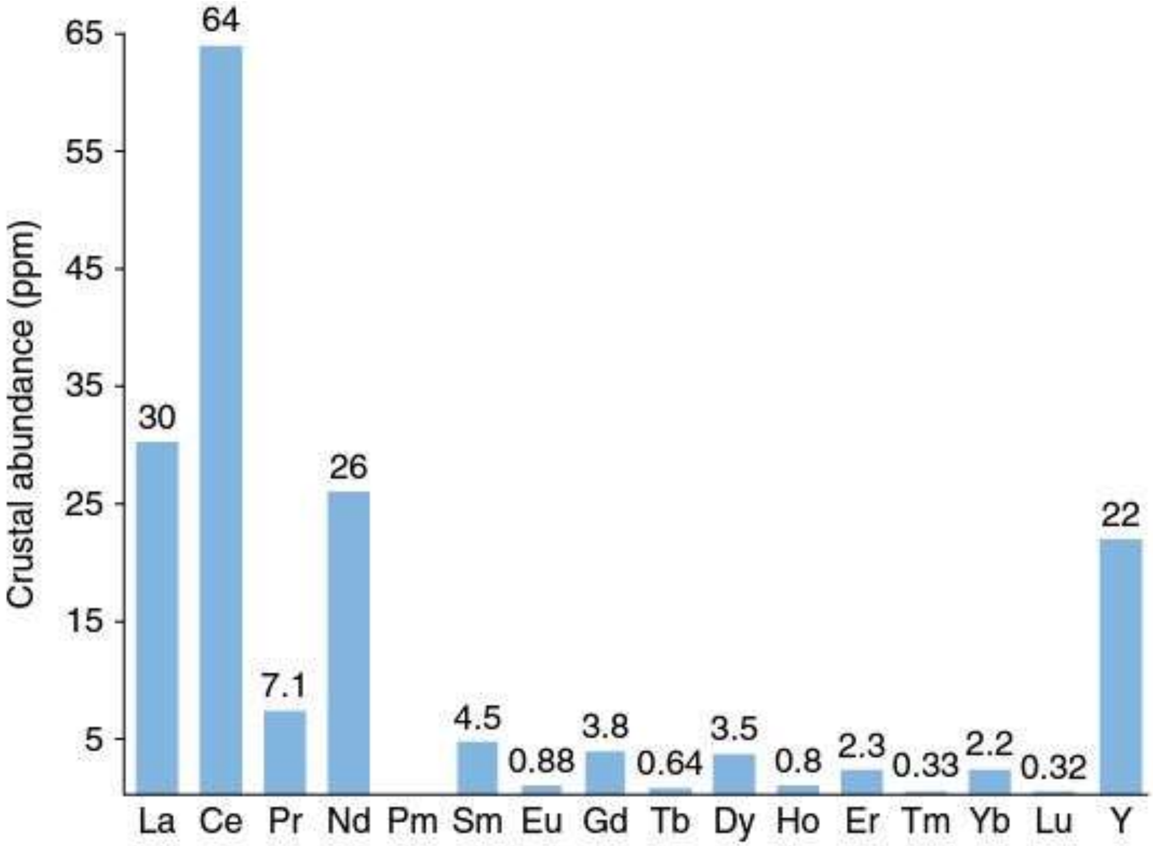


Figure 13.2 Crustal abundances of rare earth elements (Data from Taylor and McClennan, 1985). The light rare earths, lanthanum (La), cerium (Ce) and neodymium (Nd), are the most abundant rare earth elements in the Earth's crust.

REE – geochemical properties

- They are a group of 17 metallic elements (15 lanthanides + Sc and Y), with similar geochemical characteristics
- they are all present in nature, Pm is the most rare element
- identified and distinguished only in the twentieth century
- very similar chemical properties (ionic radii and oxidation state) → very difficult to separate
- not so “rare”: average crustal abundance 9.2 ppm
- divided in LREE (La → Eu) and HREE (Gd →Lu and Y)
- REE with even Z are more abundant than REE with odd Z
- REE are all trivalent ($^{+3}$) with the exception of Ce ($^{+4}$) and Eu ($^{+2}$) in some contexts
- as metal, they are silvery-white, malleable, ductile, reactive
- the electronic structure gives particular magnetic and optical properties
- REE (with the exception of Sc, Y, La, Yb and Lu) are strongly paramagnetic and with a strong magnetic anisotropy.

REE - ethymology

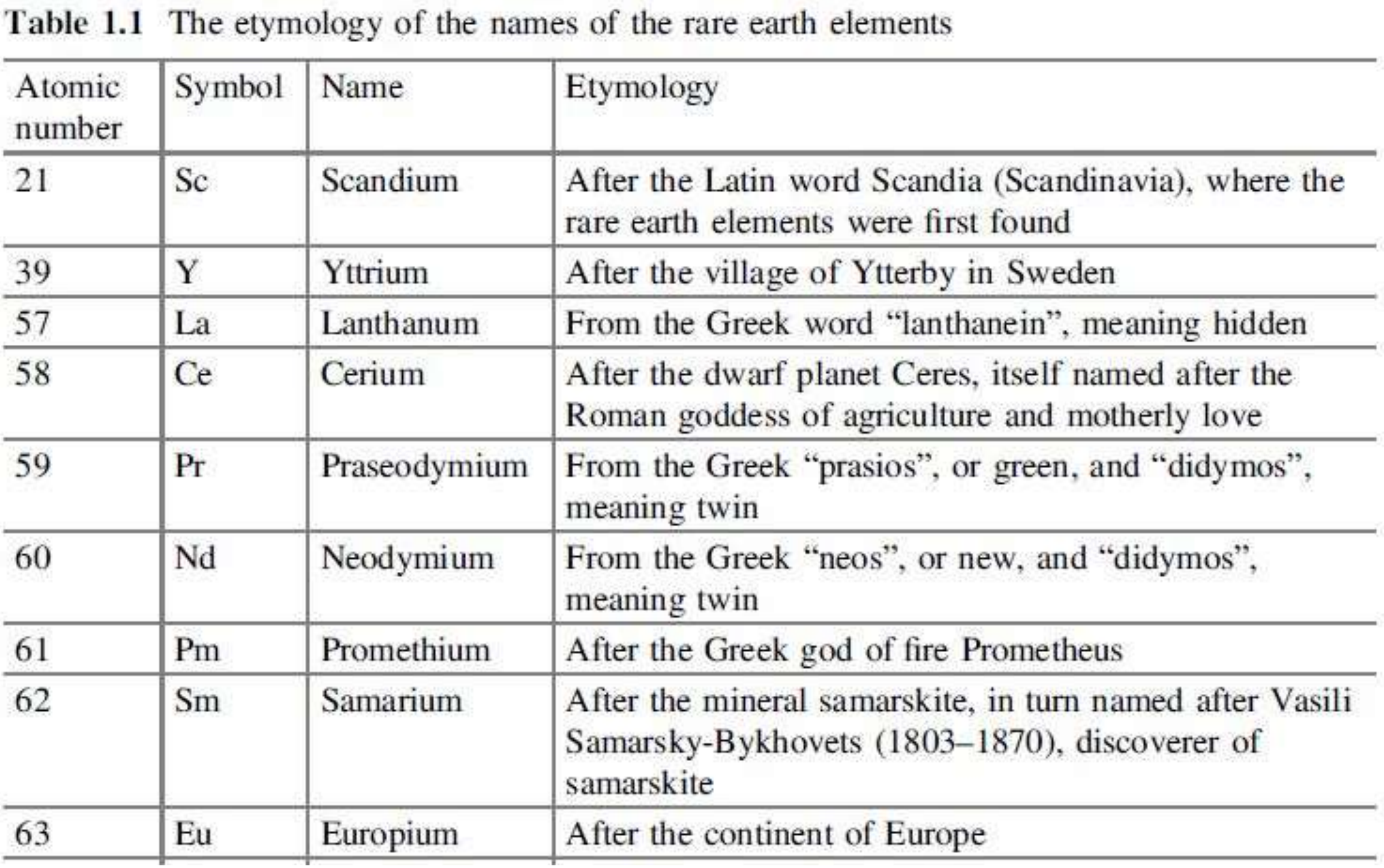
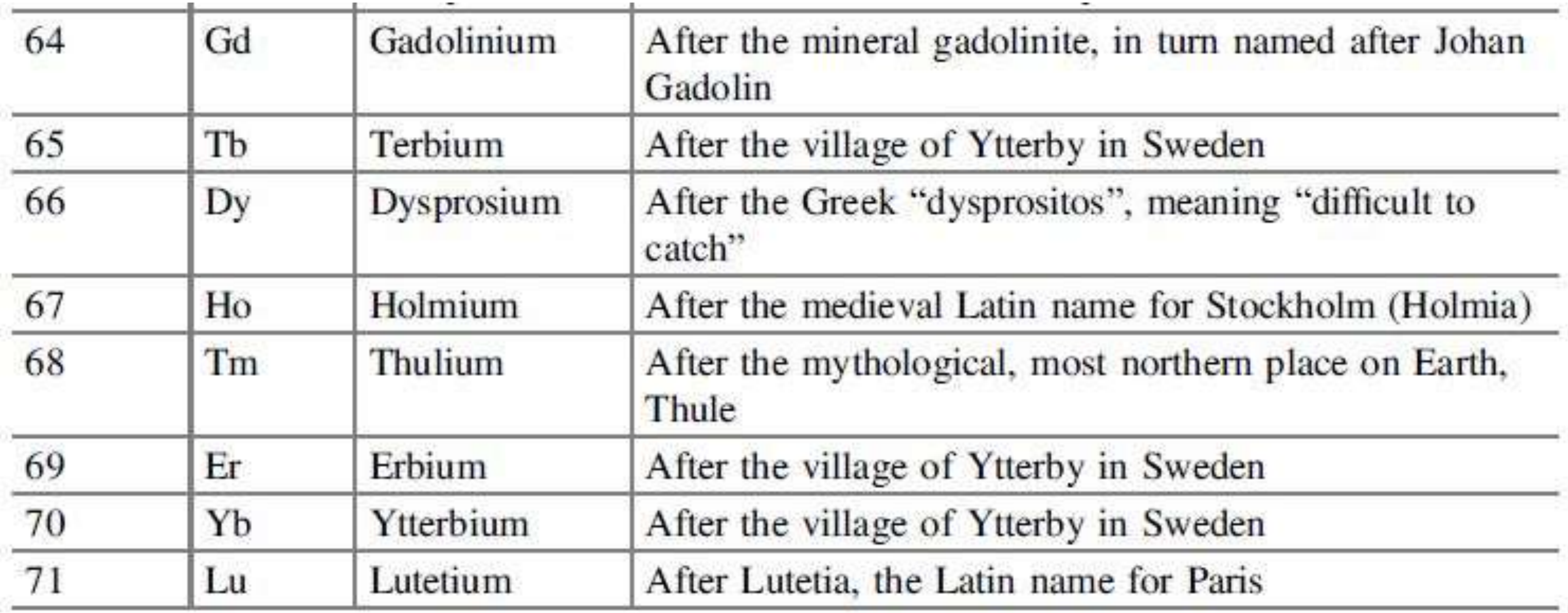


Table 1.1 The etymology of the names of the rare earth elements

Atomic number	Symbol	Name	Etymology
21	Sc	Scandium	After the Latin word Scandia (Scandinavia), where the rare earth elements were first found
39	Y	Yttrium	After the village of Ytterby in Sweden
57	La	Lanthanum	From the Greek word “lanthanein”, meaning hidden
58	Ce	Cerium	After the dwarf planet Ceres, itself named after the Roman goddess of agriculture and motherly love
59	Pr	Praseodymium	From the Greek “prasios”, or green, and “didymos”, meaning twin
60	Nd	Neodymium	From the Greek “neos”, or new, and “didymos”, meaning twin
61	Pm	Promethium	After the Greek god of fire Prometheus
62	Sm	Samarium	After the mineral samarskite, in turn named after Vasili Samarsky-Bykhovets (1803–1870), discoverer of samarskite
63	Eu	Europium	After the continent of Europe

REE - ethymology



64	Gd	Gadolinium	After the mineral gadolinite, in turn named after Johan Gadolin
65	Tb	Terbium	After the village of Ytterby in Sweden
66	Dy	Dysprosium	After the Greek “dysprositos”, meaning “difficult to catch”
67	Ho	Holmium	After the medieval Latin name for Stockholm (Holmia)
68	Tm	Thulium	After the mythological, most northern place on Earth, Thule
69	Er	Erbium	After the village of Ytterby in Sweden
70	Yb	Ytterbium	After the village of Ytterby in Sweden
71	Lu	Lutetium	After Lutetia, the Latin name for Paris

REE – selected properties

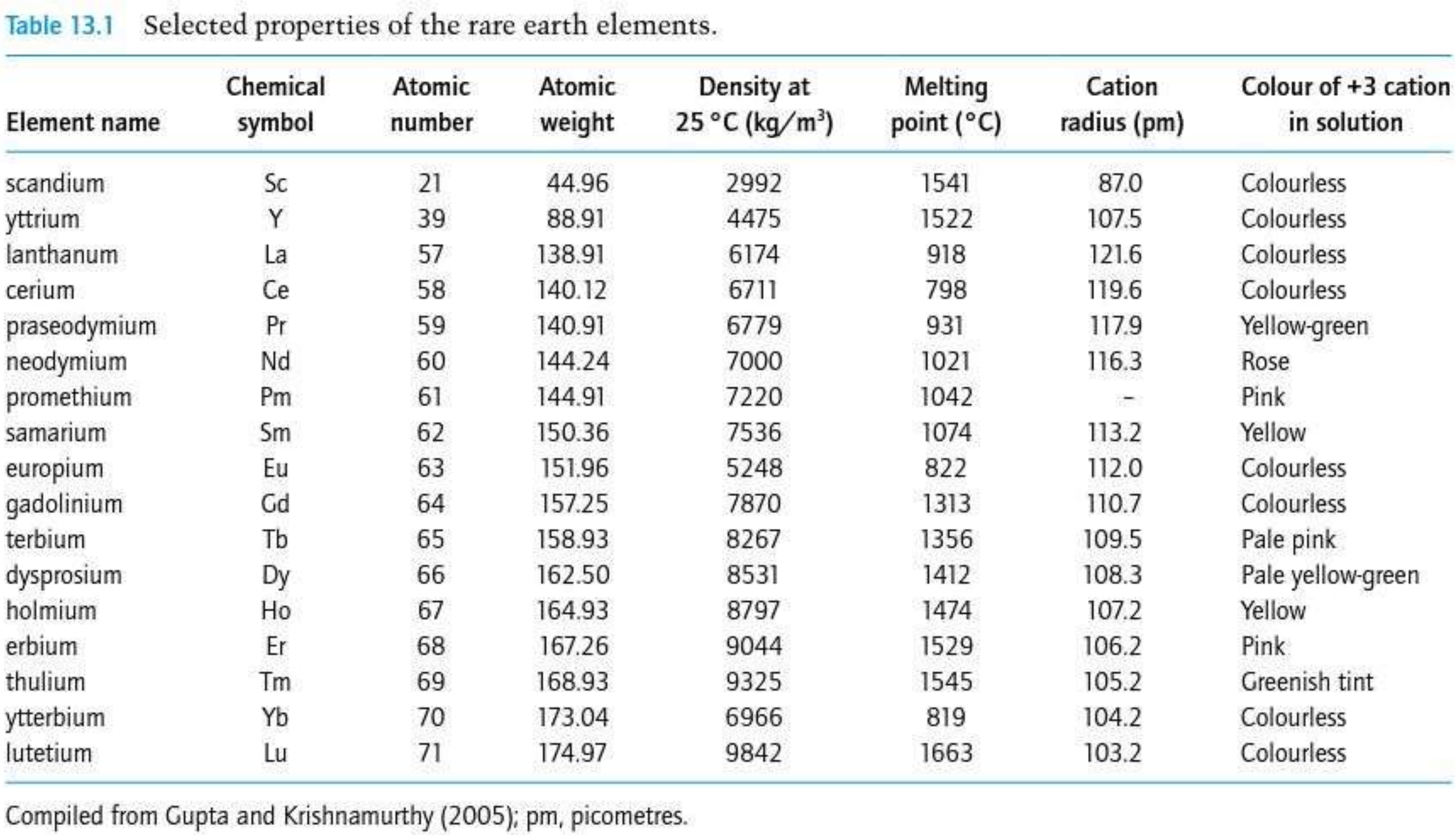
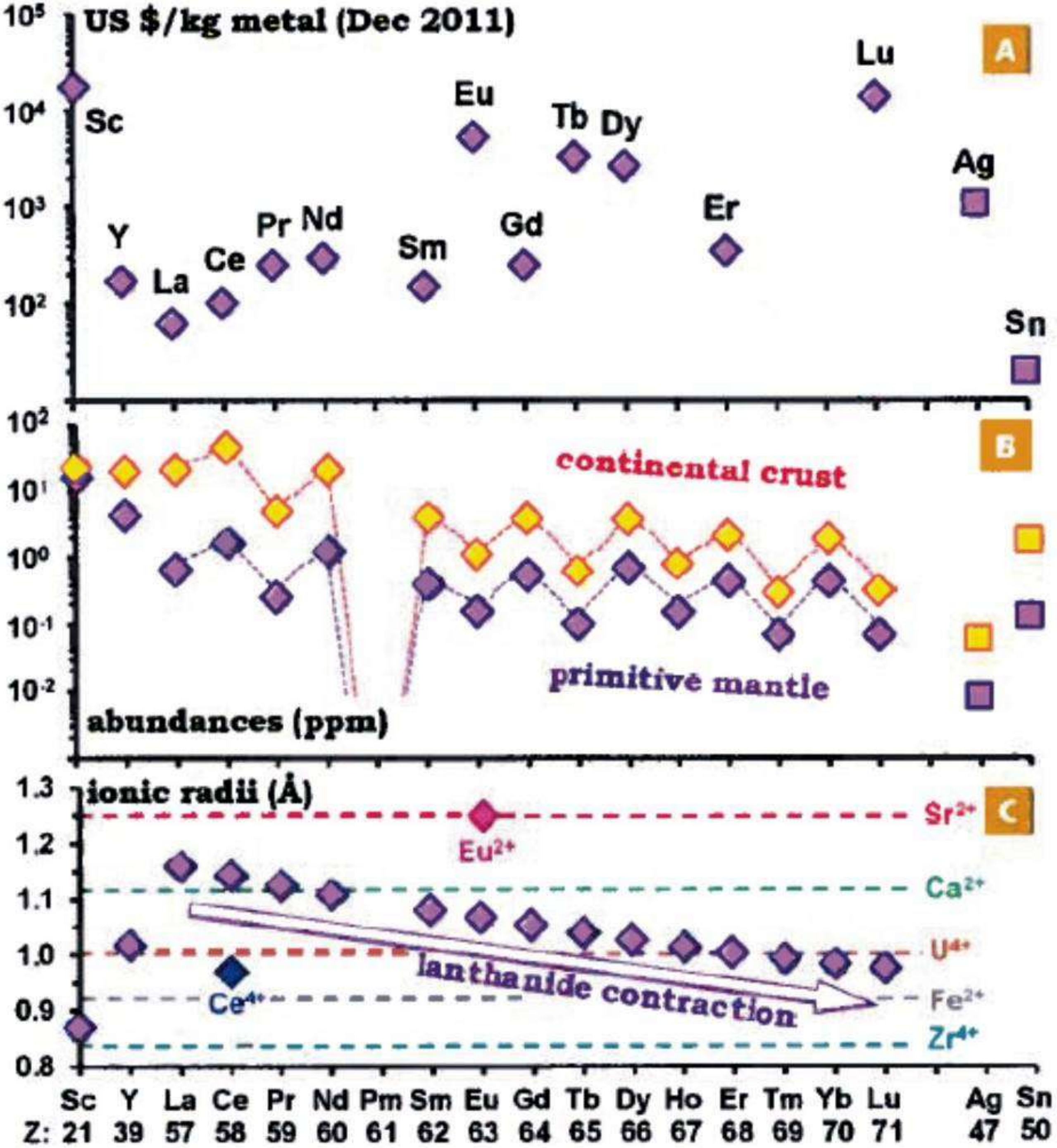


Table 13.1 Selected properties of the rare earth elements.

Element name	Chemical symbol	Atomic number	Atomic weight	Density at 25 °C (kg/m^3)	Melting point (°C)	Cation radius (pm)	Colour of +3 cation in solution
scandium	Sc	21	44.96	2992	1541	87.0	Colourless
yttrium	Y	39	88.91	4475	1522	107.5	Colourless
lanthanum	La	57	138.91	6174	918	121.6	Colourless
cerium	Ce	58	140.12	6711	798	119.6	Colourless
praseodymium	Pr	59	140.91	6779	931	117.9	Yellow-green
neodymium	Nd	60	144.24	7000	1021	116.3	Rose
promethium	Pm	61	144.91	7220	1042	–	Pink
samarium	Sm	62	150.36	7536	1074	113.2	Yellow
europium	Eu	63	151.96	5248	822	112.0	Colourless
gadolinium	Gd	64	157.25	7870	1313	110.7	Colourless
terbium	Tb	65	158.93	8267	1356	109.5	Pale pink
dysprosium	Dy	66	162.50	8531	1412	108.3	Pale yellow-green
holmium	Ho	67	164.93	8797	1474	107.2	Yellow
erbium	Er	68	167.26	9044	1529	106.2	Pink
thulium	Tm	69	168.93	9325	1545	105.2	Greenish tint
ytterbium	Yb	70	173.04	6966	819	104.2	Colourless
lutetium	Lu	71	174.97	9842	1663	103.2	Colourless

Compiled from Gupta and Krishnamurthy (2005); pm, picometres.


US $/kg metal (Dec 2011)
A
10^5
10^4
10^3
10^2
Sc
Y
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Er
Lu
Ag
Sn
B
10^2
10^1
10^0
10^{-1}
10^{-2}
continental crust
primitive mantle
abundances (ppm)
C
ionic radii (Å)
1.3
1.2
1.1
1.0
0.9
0.8
Sr^{2+}
Eu^{2+}
Ca^{2+}
U^{4+}
Ce^{4+}
Fe^{2+}
Zr^{4+}
lanthanide contraction
Sc Y La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Ag Sn
Z: 21 39 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 47 50

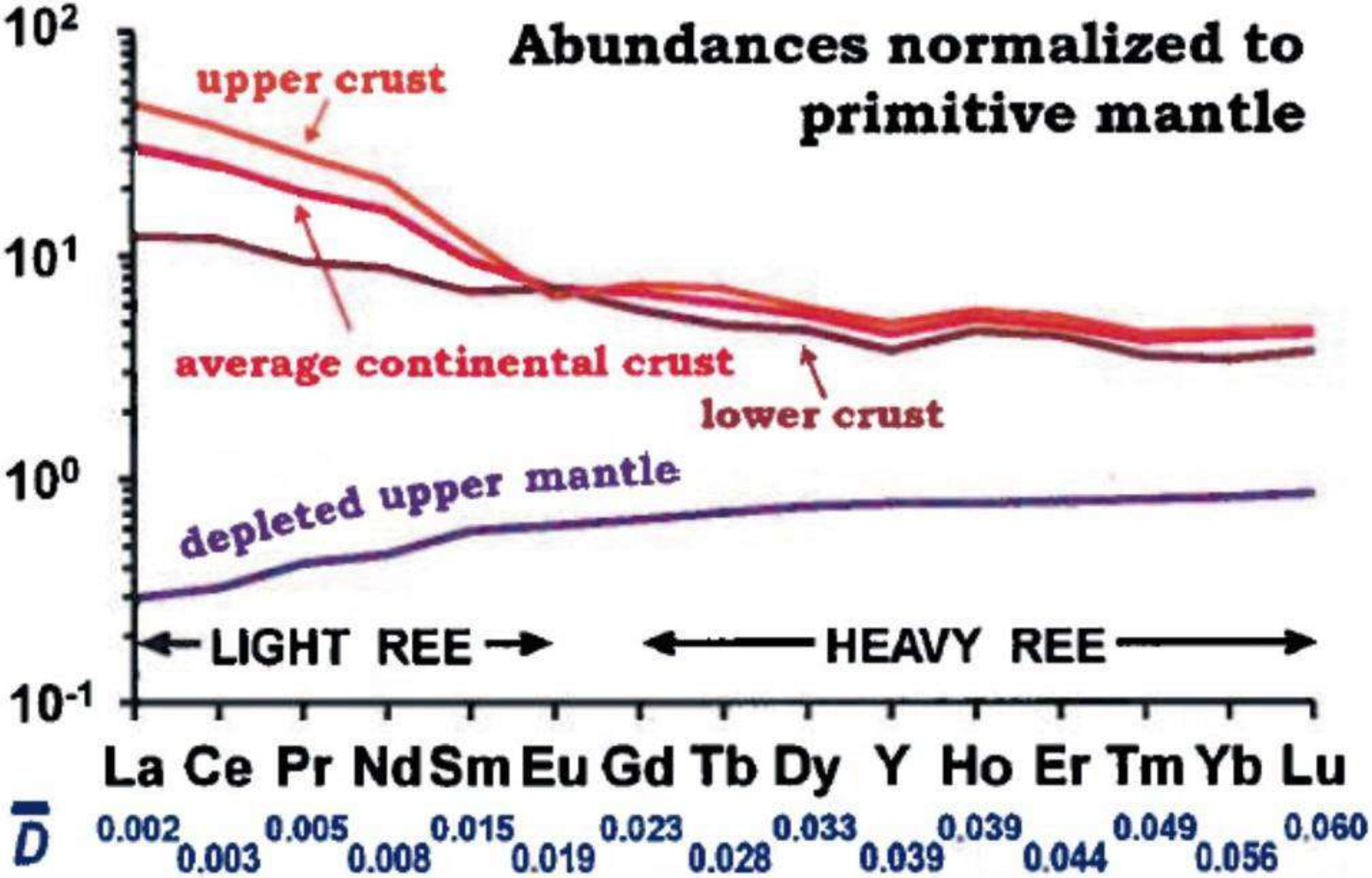


FIGURE 3 REE abundances in the depleted mantle (Workman and Hart 2005) and continental crust (Rudnick and Gao 2003) normalized to the composition of the primitive mantle (McDonough and Sun 1995). Bulk rock–melt partition coefficients ($\bar{D}$), calculated for a typical mantle peridotite, are given below the respective REEs. Note the gradual increase in compatibility from La to Lu (i.e. the decreasing tendency to partition into a melt).

REE minerals

REM Mineral	Formula	REO content (wt.%)
Aeschynite-(Ce)	$(Ce, Ca, Fe, Th)(Ti, Nb)_2(O, OH)_6$	32
Allanite-(Ce)	$(Ce, Ca, Y)_2(Al, Fe^{3+})3(SiO_4)_3OH$	38
Apatite	$Ca_5(PO_4)_3(F, Cl, OH)$	19
Bastnäsite-(Ce)	**$(Ce, La)(CO_3)F$**	**75**
Brannerite	$(U, Ca, Y, Ce)(Ti, Fe)_2O_6$	9
Britholite-(Ce)	$(Ce, Ca)_5(SiO_4, PO_4)_3(OH, F)$	32
Cebaite-(Ce)	$Ba_3Ce_2(CO_3)_5F_2$	32
Eudialyte	$Na_4(Ca, Ce)_2(Fe^{2+}, Mn, Y) ZrSi_80_{22}(OH,Cl)_2$	9
Euxenite-(Y)	$(Y, Ca, Ce, U, Th)(Nb, Ta, Ti)_2O_6$	24
Fergusonite-(Ce)	$(Ce, La, Nd)NbO_4$	53
Florencite-(Ce)	$CeAl_3(PO_4)_2(OH)_6$	32
Gadolinite-(Ce)	$(Ce, La, Nd, Y)_2Fe^{2+}Be_2Si_2O_{10}$	60
Huanghoite-(Ce)	$BaCe(CO_3)_2F$	39
Kainosite-(Y)	$Ca_2(Y, Ce)_2Si_4O_{12}CO_3H_2O$	38
Knopite	$(Ca, Ti, Ce_2)O_3$	n.d.
Liparite	$(Ce, La, Na, Ca, Sr)(Ti, Nb)O_3$	30
Monazite-(Ce)	**$(Ce, La, Nd, Th)PO_4$**	**65**
Parisite-(Ce)	$Ca(Ce, La)_2(CO_3)_3F_2$	61
Samarskite-(Y)	$(Y, Ce,U,Fe^{3+})_3(Nb,Ta,Ti)_5O_{16}$	24
Synchysite-(Ce)	$Ca(Ce, La)(CO_3)_2F$	51
Xenotime	**YPO_4**	**61**
Yttrocerite	$(Ca, Ce, Y, La)F_3.nH_2O$	53

REM – rare earth minerals

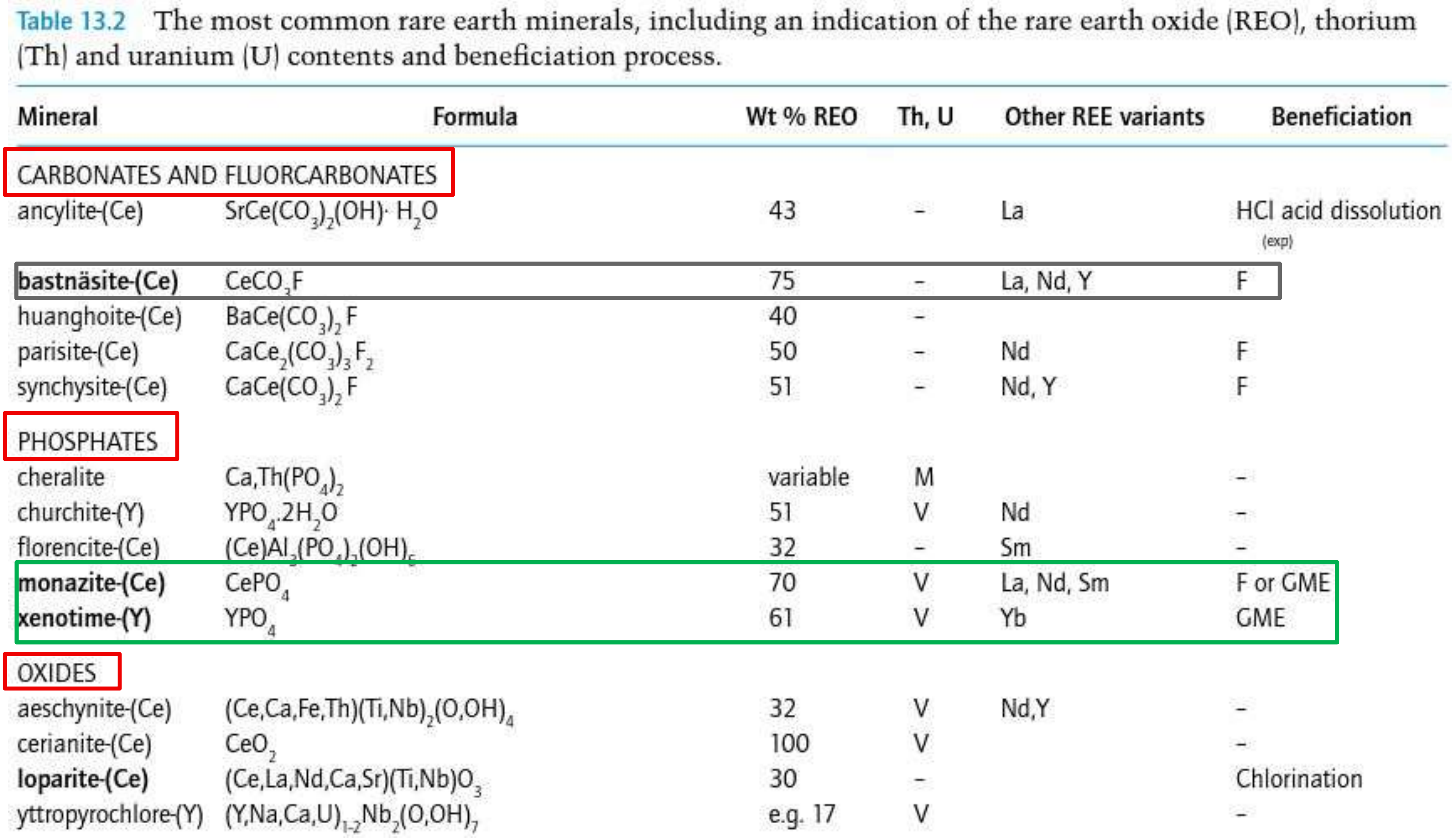


Table 13.2 The most common rare earth minerals, including an indication of the rare earth oxide (REO), thorium (Th) and uranium (U) contents and beneficiation process.

Mineral	Formula	Wt % REO	Th, U	Other REE variants	Beneficiation
CARBONATES AND FLUORCARBONATES					
ancylite-(Ce)	$SrCe(CO_3)_2(OH)\cdot H_2O$	43	–	La	HCl acid dissolution (exp)
bastnäsite-(Ce)	$CeCO_3F$	75	–	La, Nd, Y	F
huanghoite-(Ce)	$BaCe(CO_3)_2F$	40	–		
parisite-(Ce)	$CaCe_2(CO_3)_3F_2$	50	–	Nd	F
synchysite-(Ce)	$CaCe(CO_3)_2F$	51	–	Nd, Y	F
PHOSPHATES					
cheralite	$Ca,Th(PO_4)_2$	variable	M		–
churchite-(Y)	$YPO_4.2H_2O$	51	V	Nd	–
florencite-(Ce)	$(Ce)Al_3(PO_4)_2(OH)_6$	32	–	Sm	–
monazite-(Ce)	$CePO_4$	70	V	La, Nd, Sm	F or GME
xenotime-(Y)	YPO_4	61	V	Yb	GME
OXIDES					
aeschynite-(Ce)	$(Ce,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_4$	32	V	Nd,Y	–
cerianite-(Ce)	CeO_2	100	V		–
loparite-(Ce)	$(Ce,La,Nd,Ca,Sr)(Ti,Nb)O_3$	30	–		Chlorination
yttropyrochlore-(Y)	$(Y,Na,Ca,U)_{1\text{-}2}Nb_2(O,OH)_7$	e.g. 17	V		–

REM – rare earth minerals

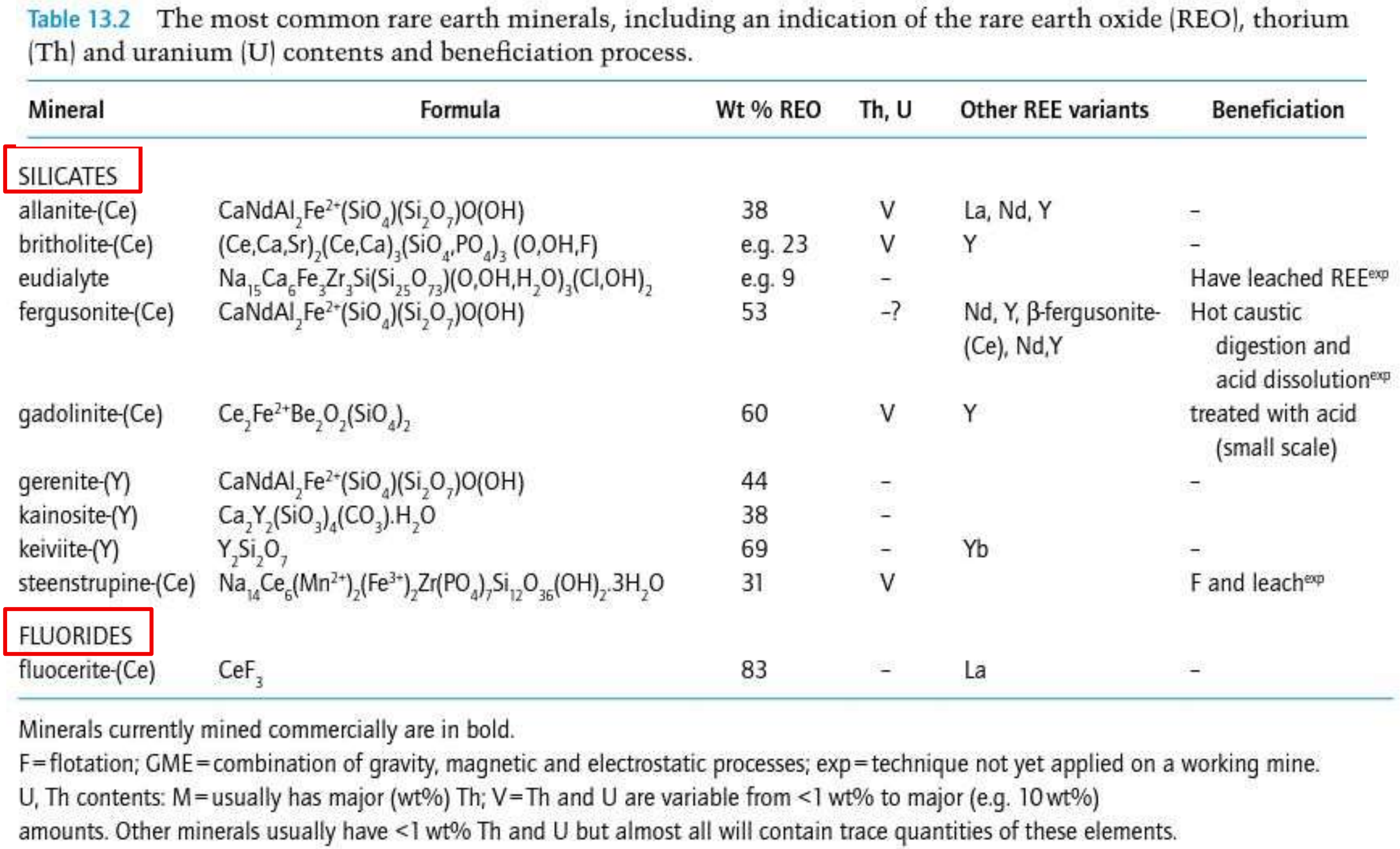


Table 13.2 The most common rare earth minerals, including an indication of the rare earth oxide (REO), thorium (Th) and uranium (U) contents and beneficiation process.

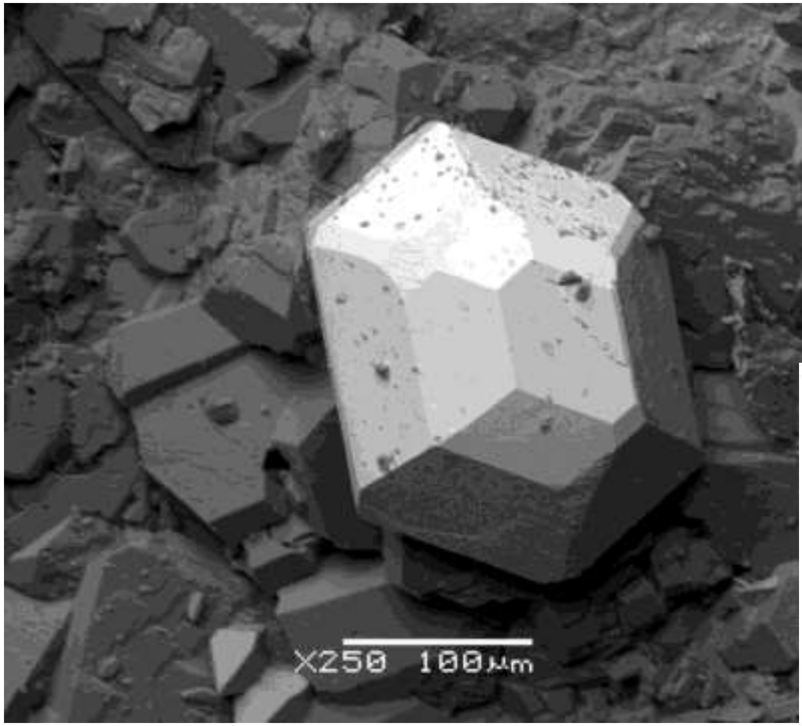
Mineral	Formula	Wt % REO	Th, U	Other REE variants	Beneficiation
SILICATES					
allanite-(Ce)	$CaNdAl_2Fe^{2+}(SiO_4)(Si_2O_7)O(OH)$	38	V	La, Nd, Y	–
britholite-(Ce)	$(Ce,Ca,Sr)_2(Ce,Ca)_3(SiO_4,PO_4)_3\,(O,OH,F)$	e.g. 23	V	Y	–
eudialyte	$Na_{15}Ca_6Fe_3Zr_3Si(Si_{25}O_{73})(O,OH,H_2O)_3(Cl,OH)_2$	e.g. 9	–		Have leached REE^{exp}
fergusonite-(Ce)	$CaNdAl_2Fe^{2+}(SiO_4)(Si_2O_7)O(OH)$	53	–?	Nd, Y, β-fergusonite-(Ce), Nd,Y	Hot caustic digestion and acid dissolution^{exp}
gadolinite-(Ce)	$Ce_2Fe^{2+}Be_2O_2(SiO_4)_2$	60	V	Y	treated with acid (small scale)
gerenite-(Y)	$CaNdAl_2Fe^{2+}(SiO_4)(Si_2O_7)O(OH)$	44	–		–
kainosite-(Y)	$Ca_2Y_2(SiO_3)_4(CO_3).H_2O$	38	–		
keiviite-(Y)	$Y_2Si_2O_7$	69	–	Yb	–
steenstrupine-(Ce)	$Na_{14}Ce_6(Mn^{2+})_2(Fe^{3+})_2Zr(PO_4)_7Si_{12}O_{36}(OH)_2.3H_2O$	31	V		F and leach^{exp}
FLUORIDES					
fluocerite-(Ce)	CeF_3	83	-	La	–

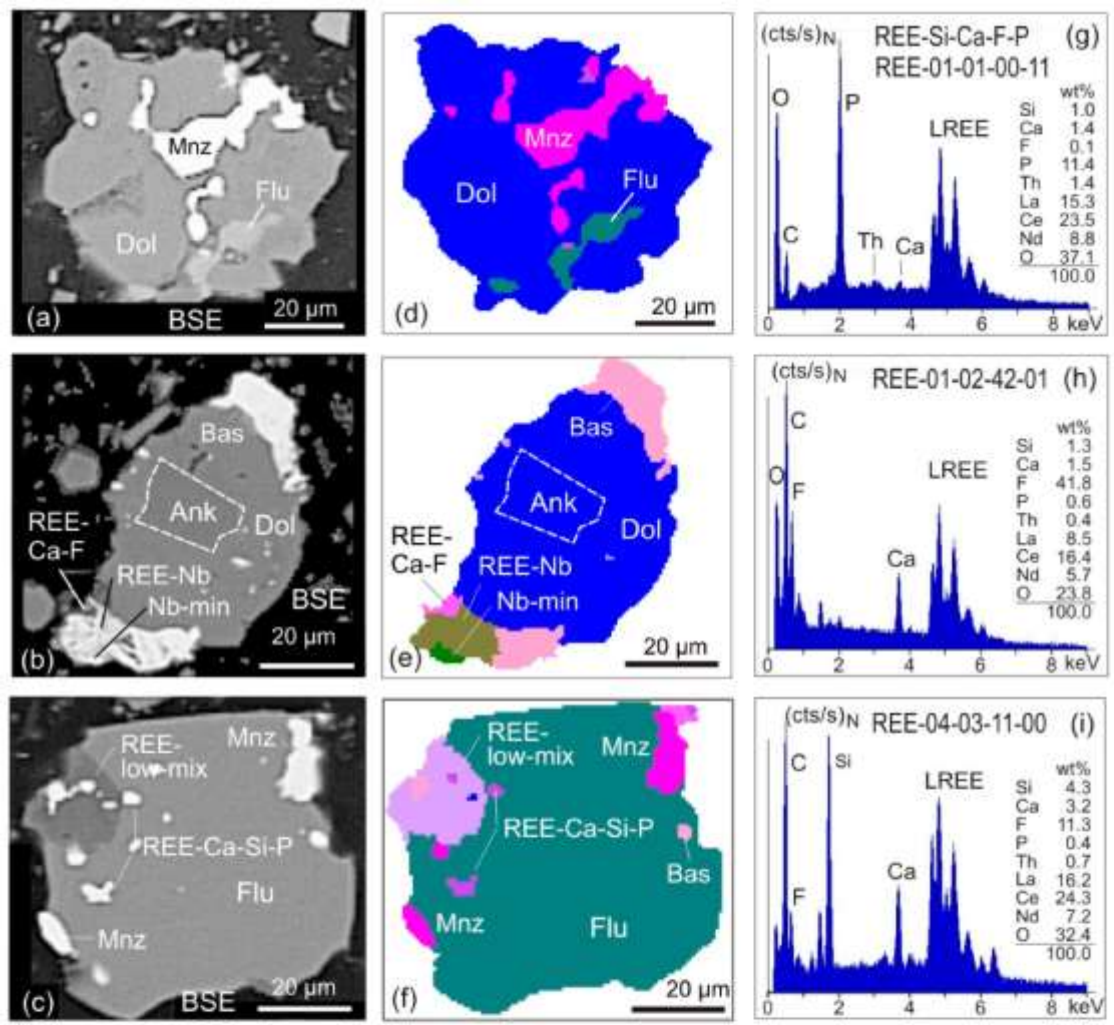
Minerals currently mined commercially are in bold.

F = flotation; GME = combination of gravity, magnetic and electrostatic processes; exp = technique not yet applied on a working mine.

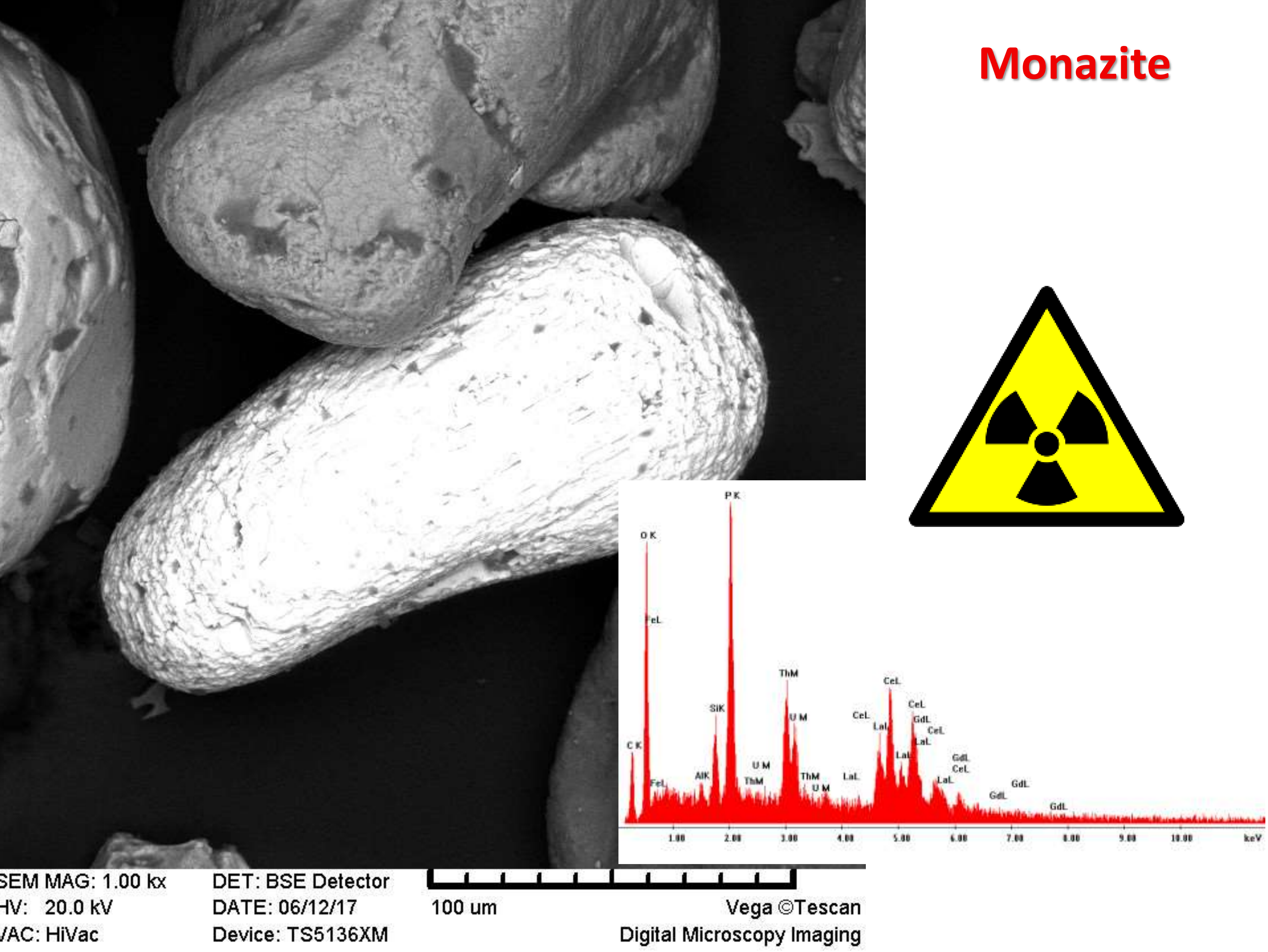
U, Th contents: M = usually has major (wt%) Th; V = Th and U are variable from <1 wt% to major (e.g. 10 wt%) amounts. Other minerals usually have <1 wt% Th and U but almost all will contain trace quantities of these elements.

Bastnaesite





Monazite


P K
O K
FeL
ThM
CeL
SiK
U M
CeL
LaL
CeL
GdL
CeL
LaL
C K
LaL
U M
GdL
CeL
AlK
FeL
ThM
ThM
U M
LaL
LaL
GdL
GdL
GdL
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
keV
SEM MAG: 1.00 kx
HV: 20.0 kV
VAC: HiVac
DET: BSE Detector
DATE: 06/12/17
Device: TS5136XM
100 um
Vega ©Tescan
Digital Microscopy Imaging

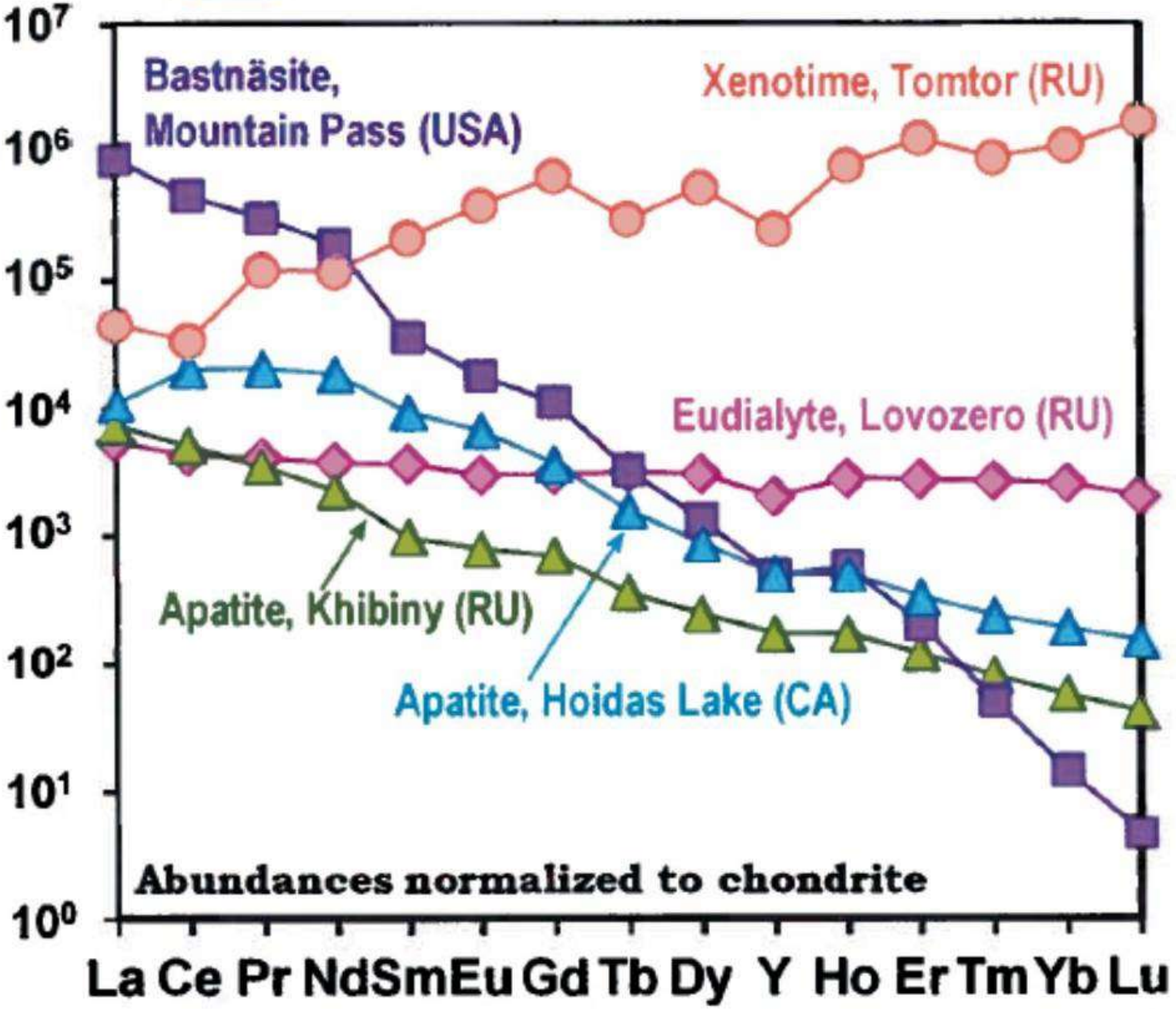


Figure 4 Chondrite-normalized REE profiles of selected minerals (Chakhmouradian and Reguir, unpublished data), including some typical constituents of REE ores and minerals that are currently investigated as potential industrial sources of rare earths (abbreviations as in Table 1; chondrite values from Anders and Grevesse 1989)

REM – rare earth minerals

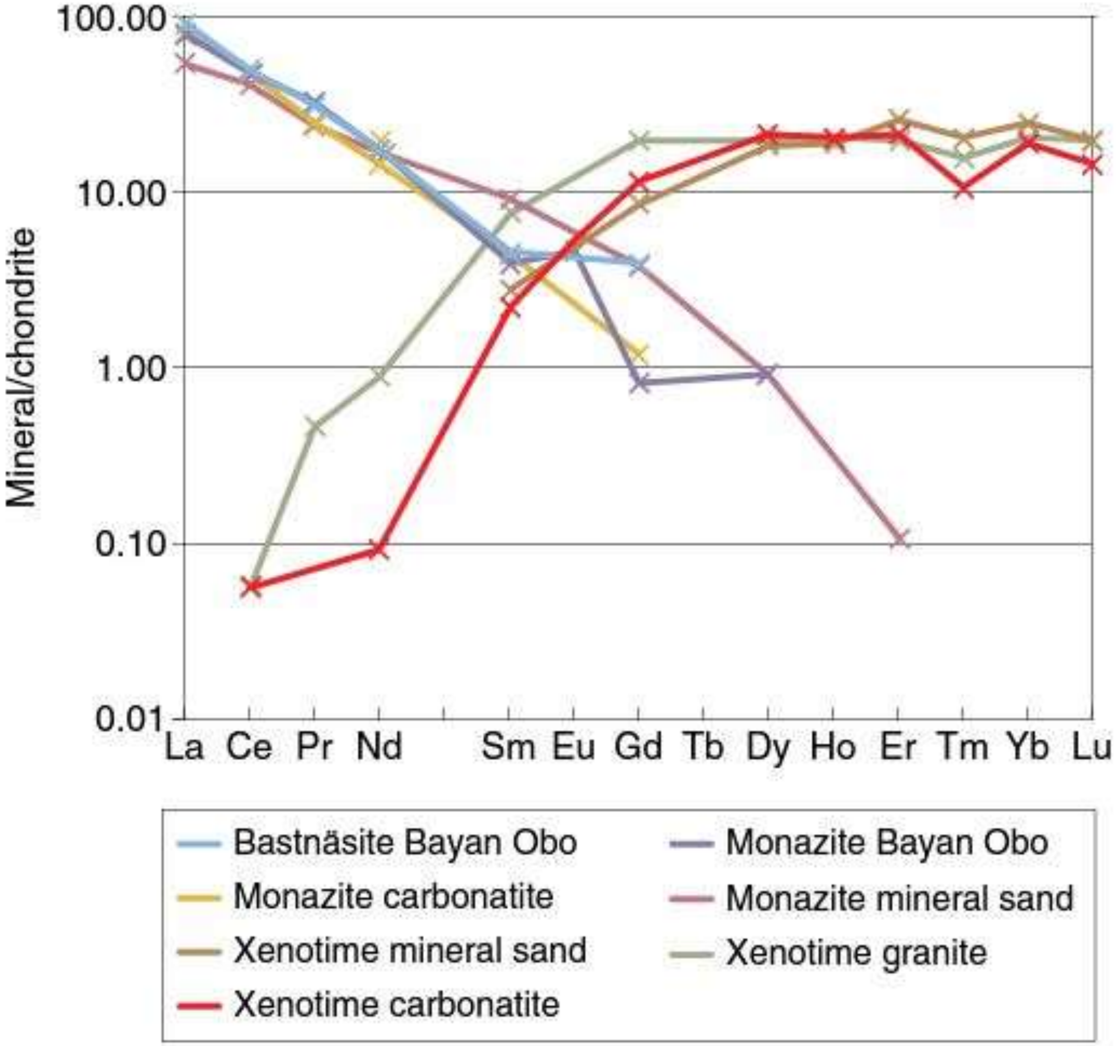


Figure 13.3 Compositions of the most common light REE minerals, bastnäsite-(Ce) and monazite-(Ce), and the most common heavy REE mineral, xenotime-(Y). Following usual precedent, values are divided by values of a chondrite meteorite (McDonough and Sun, 1995) in order to remove the Oddo-Harkins 'zig-zag' effect. (Data from Förster (1998), Smith et al. (2000), van Emden et al. (1997), Wall and Mariano (1996), Wall et al. (2008).)

REE ore deposits

Distributed in a wide range of magmatic, metamorphic and sedimentary rocks.

Geological environments with REE concentrations are essentially two:

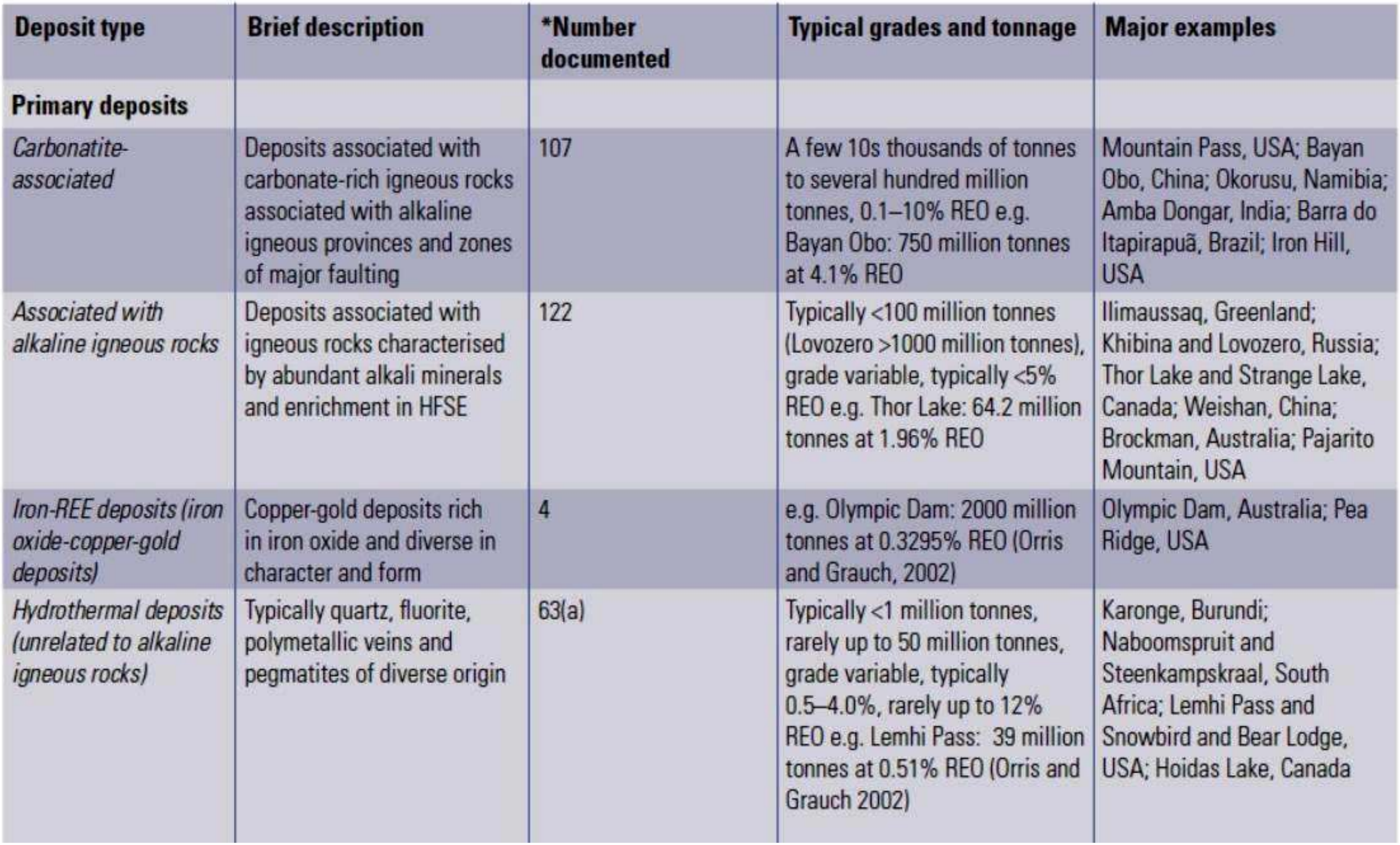
- Primary ore deposits

*linked to **magmatic** and **hydrothermal** processes*

- Secondary ore deposits

*linked to **sedimentary** processes and **meteoric alteration.***

Primary ore deposits



Deposit type	Brief description	*Number documented	Typical grades and tonnage	Major examples
Primary deposits				
Carbonatite-associated	Deposits associated with carbonate-rich igneous rocks associated with alkaline igneous provinces and zones of major faulting	107	A few 10s thousands of tonnes to several hundred million tonnes, 0.1–10% REO e.g. Bayan Obo: 750 million tonnes at 4.1% REO	Mountain Pass, USA; Bayan Obo, China; Okorusu, Namibia; Amba Dongar, India; Barra do Itapirapuã, Brazil; Iron Hill, USA
Associated with alkaline igneous rocks	Deposits associated with igneous rocks characterised by abundant alkali minerals and enrichment in HFSE	122	Typically <100 million tonnes (Lovozero >1000 million tonnes), grade variable, typically <5% REO e.g. Thor Lake: 64.2 million tonnes at 1.96% REO	Ilimaussaq, Greenland; Khibina and Lovozero, Russia; Thor Lake and Strange Lake, Canada; Weishan, China; Brockman, Australia; Pajarito Mountain, USA
Iron-REE deposits (iron oxide-copper-gold deposits)	Copper-gold deposits rich in iron oxide and diverse in character and form	4	e.g. Olympic Dam: 2000 million tonnes at 0.3295% REO (Orris and Grauch, 2002)	Olympic Dam, Australia; Pea Ridge, USA
Hydrothermal deposits (unrelated to alkaline igneous rocks)	Typically quartz, fluorite, polymetallic veins and pegmatites of diverse origin	63(a)	Typically <1 million tonnes, rarely up to 50 million tonnes, grade variable, typically 0.5–4.0%, rarely up to 12% REO e.g. Lemhi Pass: 39 million tonnes at 0.51% REO (Orris and Grauch 2002)	Karonge, Burundi; Naboomspruit and Steenkampskraal, South Africa; Lemhi Pass and Snowbird and Bear Lodge, USA; Hoidas Lake, Canada

Primary ore deposits

Linked to ***magmatic processes***

Mountain Pass carbonatitic intrusion, Colorado (USA):

"*tout-venant*" with 7-8% REE, calcite (40%), barite and celestine (25%), bastnäsite (12%), strontianite (10%), silicates (8%) and rare sulfides (galena).
Reserves about 100 Mt @ 7% REO, annual production about 20.000 t/year.

Fe-REE ore deposits, also known as *Iron Oxide Copper Gold* (IOCG) or *Olympic Dam Type* (with reference to the well-known Australian Cu-U-Ag-Au-REE deposit).

REE ore deposits are hosted in a wide variety of magmatic (both intrusive and volcanic) and sedimentary rocks.

Primary ore deposits

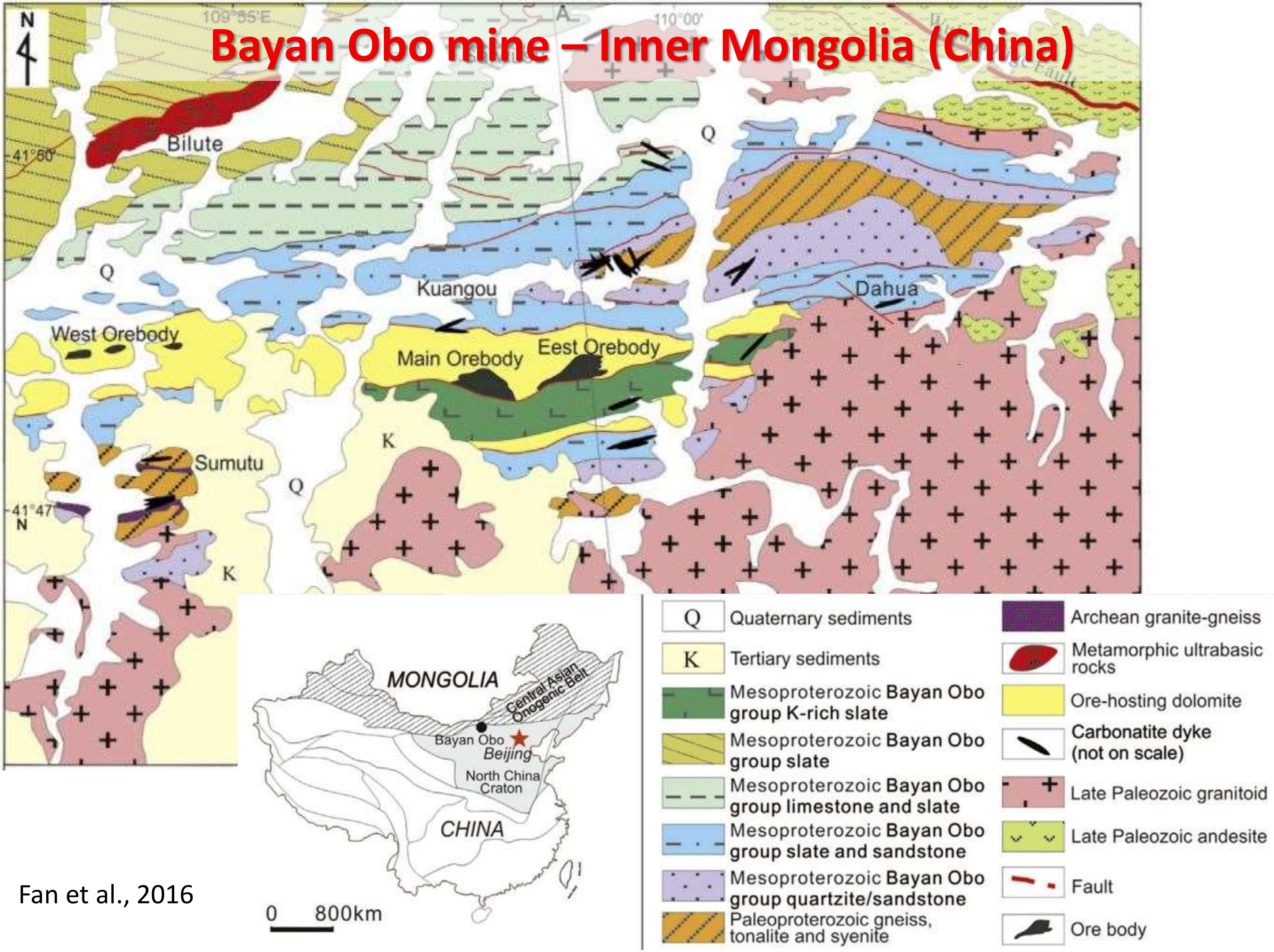
Linked to ***hydrothermal processes***

Bayan Obo, Inner Mongolia (China)

Fe deposit (10 Gt @ 32.35% Fe_2O_3) composed of three ferruginous bodies interlayered in the upper part of a dolomite formation.

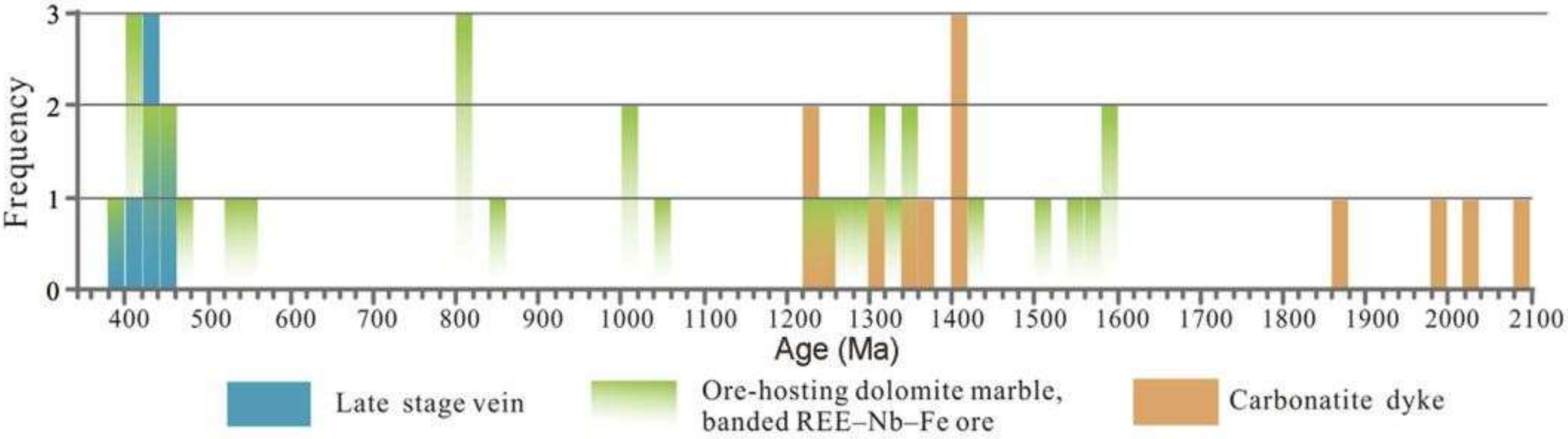
The REE mineralization, a by-product with grades about 6%, is ***stratabound***, consisting of centimetric veins of dolomite, bastnäsite and monazite, that impregnate ferruginous lenses with hematite and magnetite.

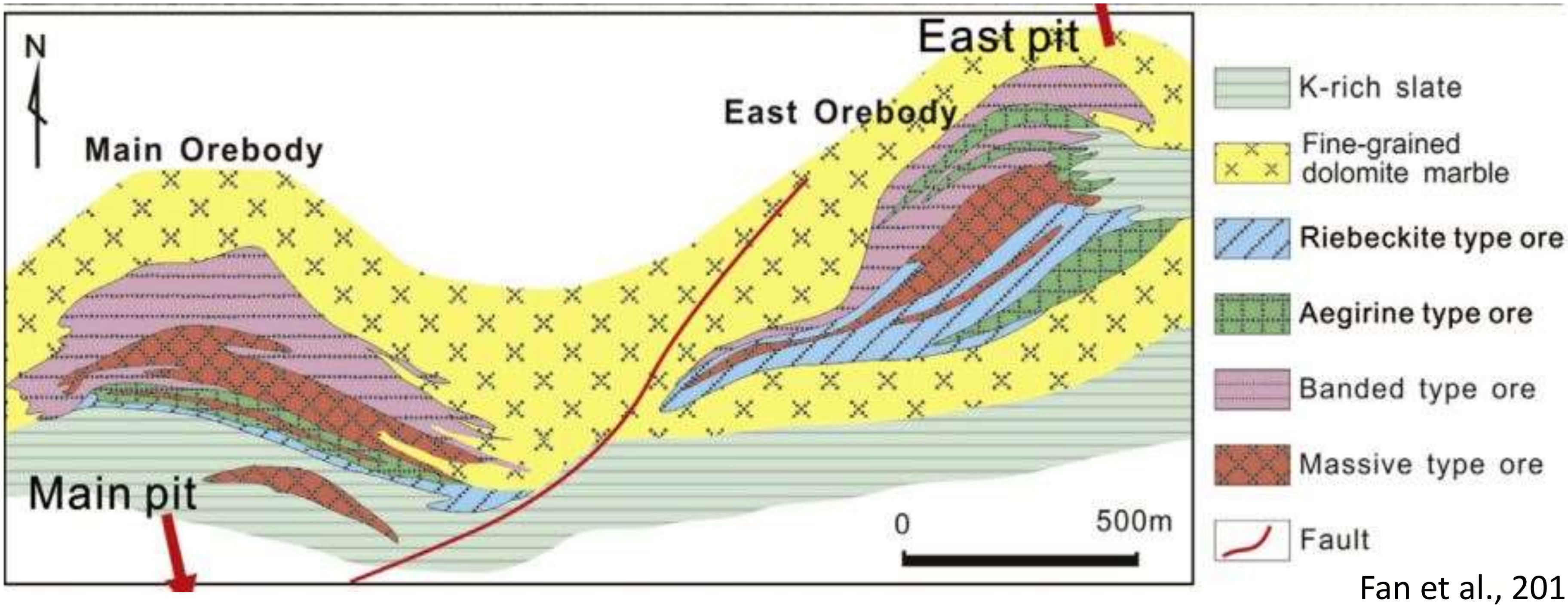
Bayan Obo mine – Inner Mongolia (China)



Fan et al., 2016

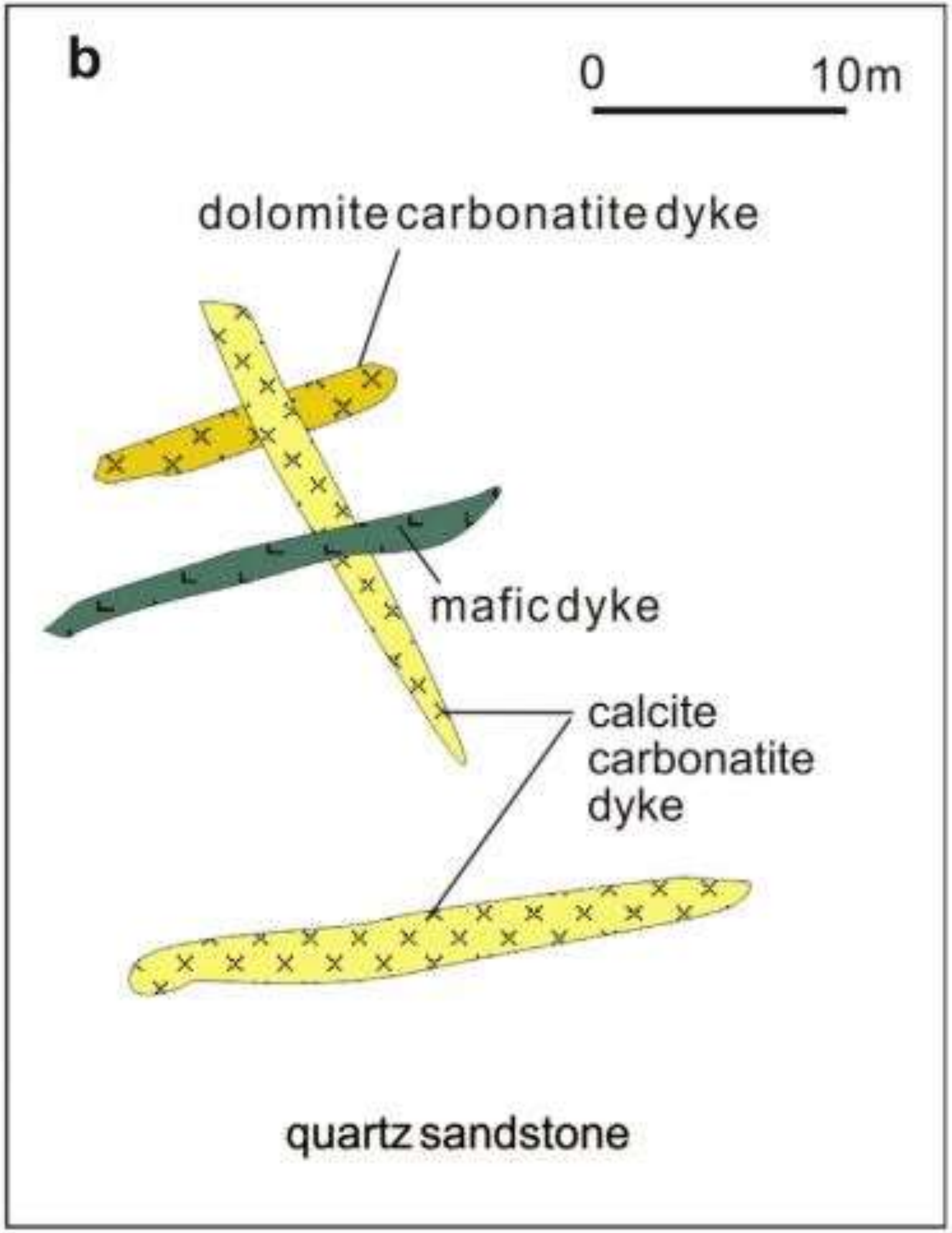
Bayan Obo mine – Inner Mongolia (China)





Fan et al., 2016

Bayan Obo mine – Inner Mongolia (China)



Fan et al., 2016

Bayan Obo ore

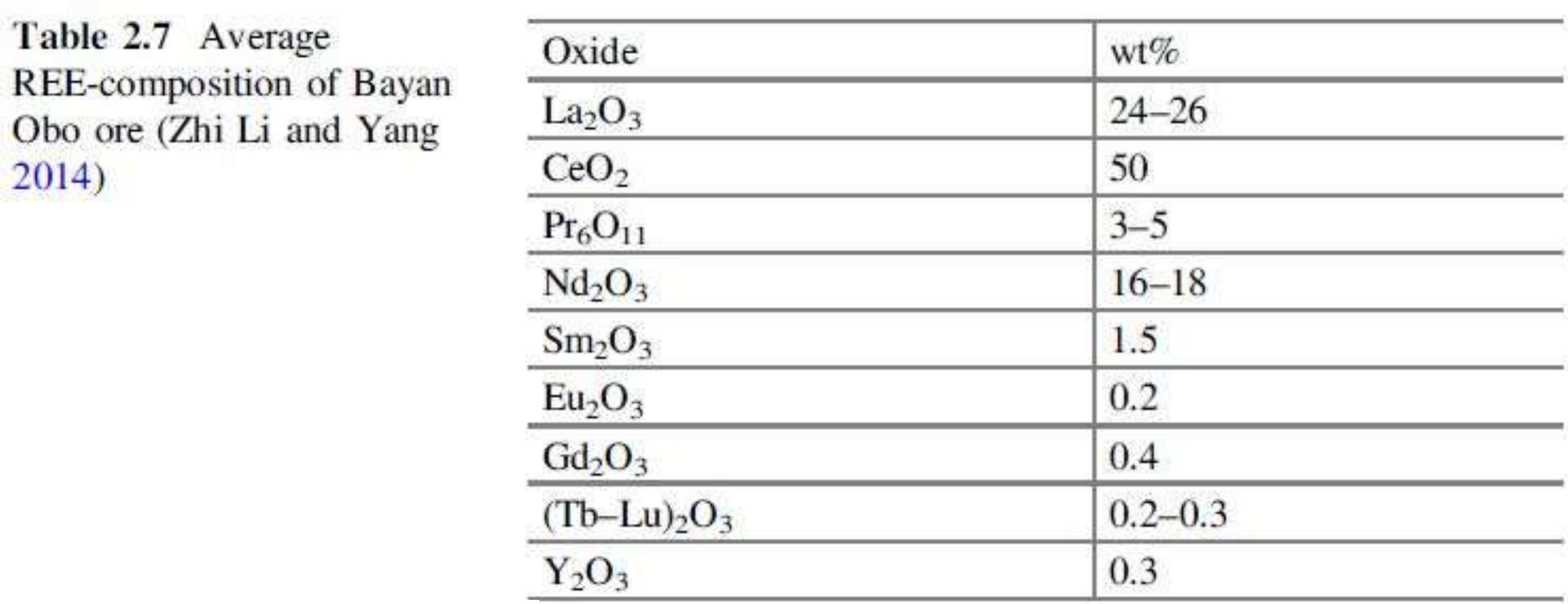
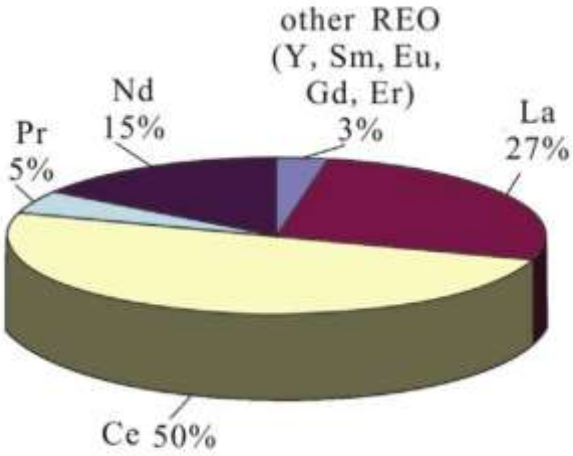


Table 2.7 Average REE-composition of Bayan Obo ore (Zhi Li and Yang 2014)

Oxide	wt%
La_2O_3	24–26
CeO_2	50
Pr_6O_{11}	3–5
Nd_2O_3	16–18
Sm_2O_3	1.5
Eu_2O_3	0.2
Gd_2O_3	0.4
$(Tb–Lu)_2O_3$	0.2–0.3
Y_2O_3	0.3



Bayan Obo mine – Inner Mongolia (China)

Bayan Obo mine – Inner Mongolia (China)

Bayan Obo mine – Inner Mongolia (China)

© Richard Jones/Sinopix

Mountain Pass Mine, Sulphide Queen Carbonatite

Major Minerals:

Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Barite	$BaSO_4$
Celestite	$SrSO_4$
Quartz	SiO_2
Bastnäsite	$(REE)CO_3F$

Abundant to Trace:

Monazite	$(REE,Th)PO_4$
Apatite	$Ca_5(PO_4)F$
Parasite	$(REE)_2Ca(CO_3)_3F_2$
Strontianite	$SrCO_3$

Widespread:

Galena	PbS
Talc	$Mg_3Si_4O_{10}(OH)_2$

Trace:

Pyrite	FeS_2

Mountain Pass mine (California, USA)

Mountain Pass mine (California, USA) ore concentrate

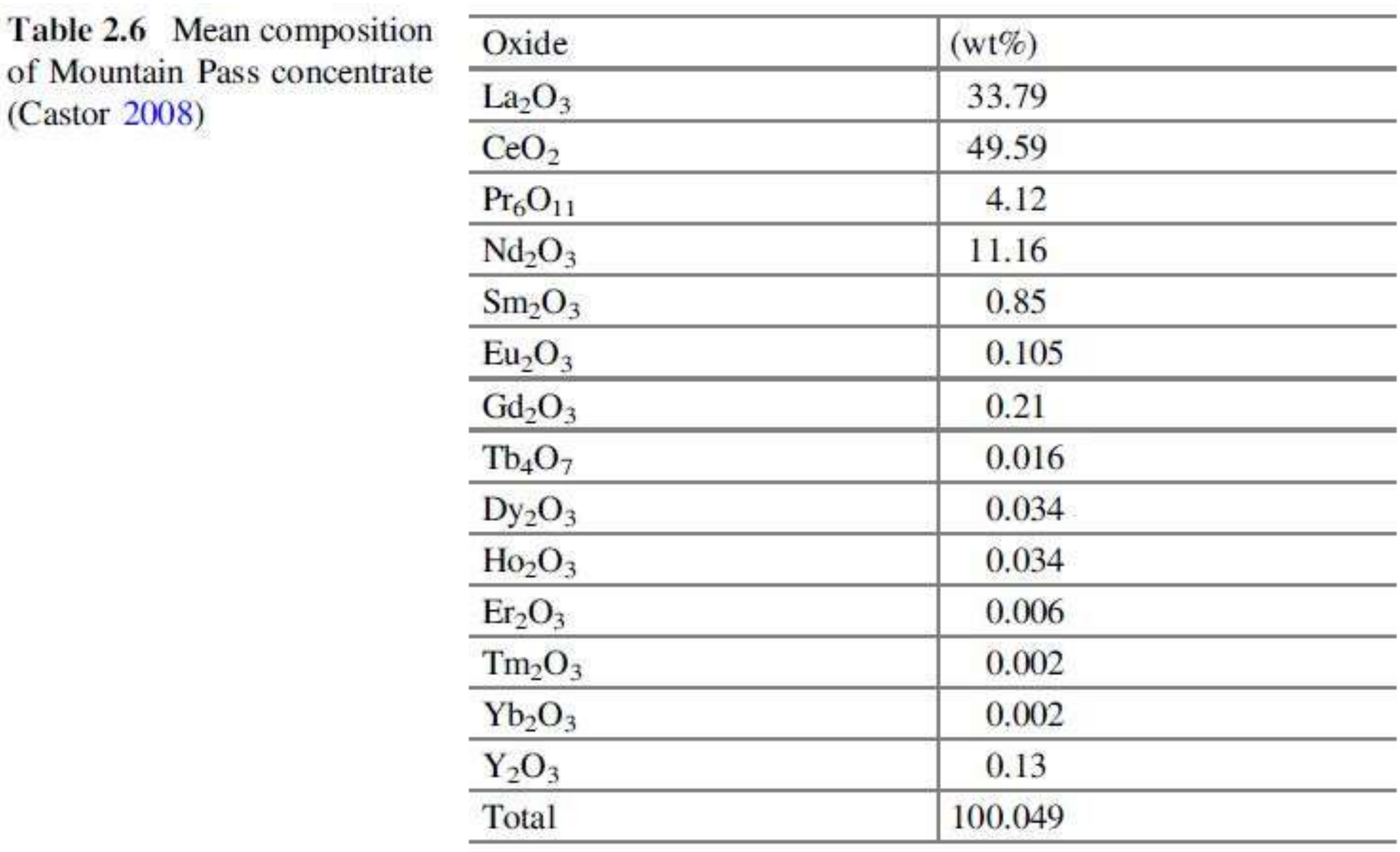
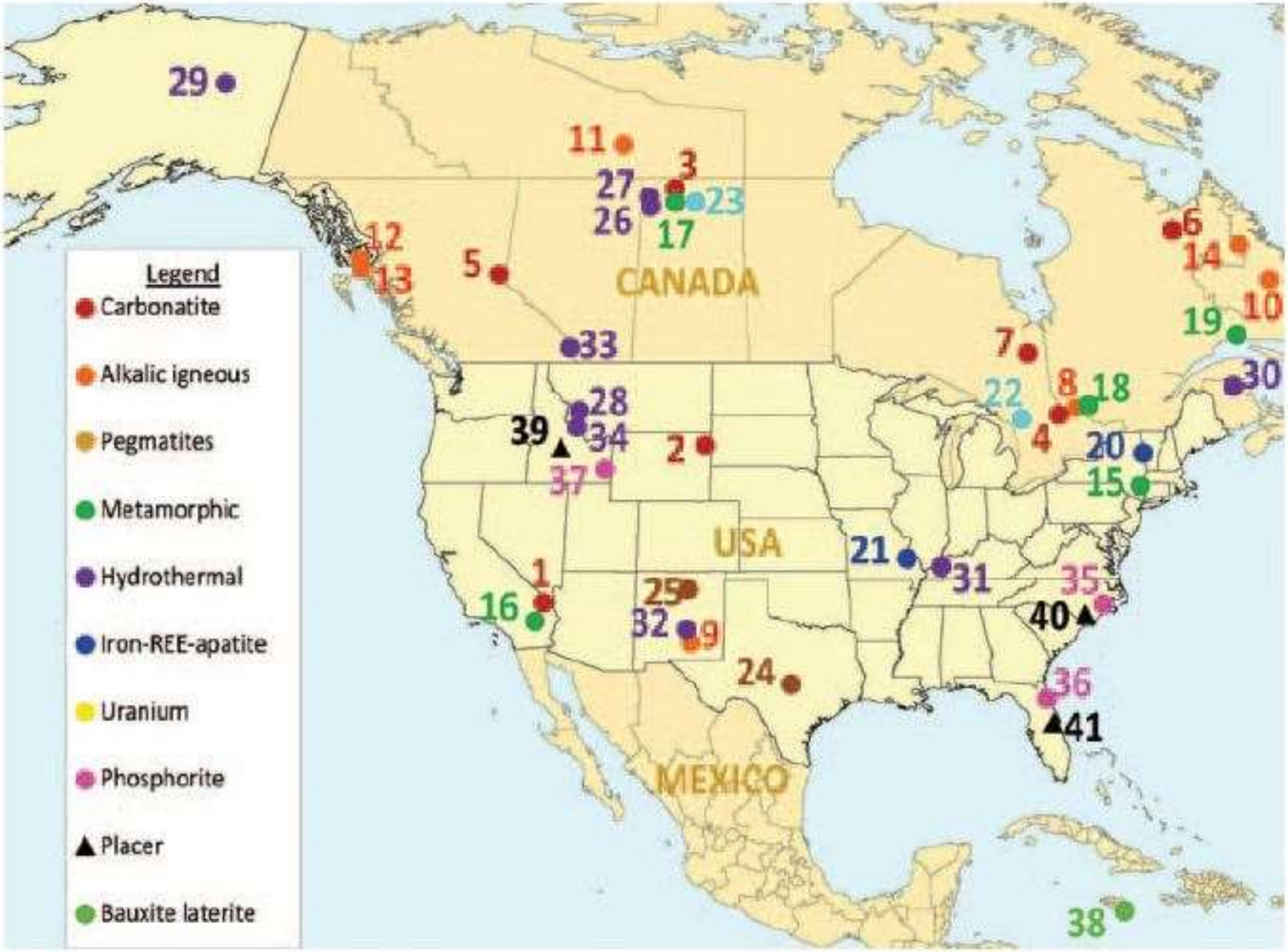


Table 2.6 Mean composition of Mountain Pass concentrate (Castor 2008)

Oxide	(wt%)
La_2O_3	33.79
CeO_2	49.59
Pr_6O_{11}	4.12
Nd_2O_3	11.16
Sm_2O_3	0.85
Eu_2O_3	0.105
Gd_2O_3	0.21
Tb_4O_7	0.016
Dy_2O_3	0.034
Ho_2O_3	0.034
Er_2O_3	0.006
Tm_2O_3	0.002
Yb_2O_3	0.002
Y_2O_3	0.13
Total	100.049

North America REE ore deposits



Secondary ore deposits

- *placers*

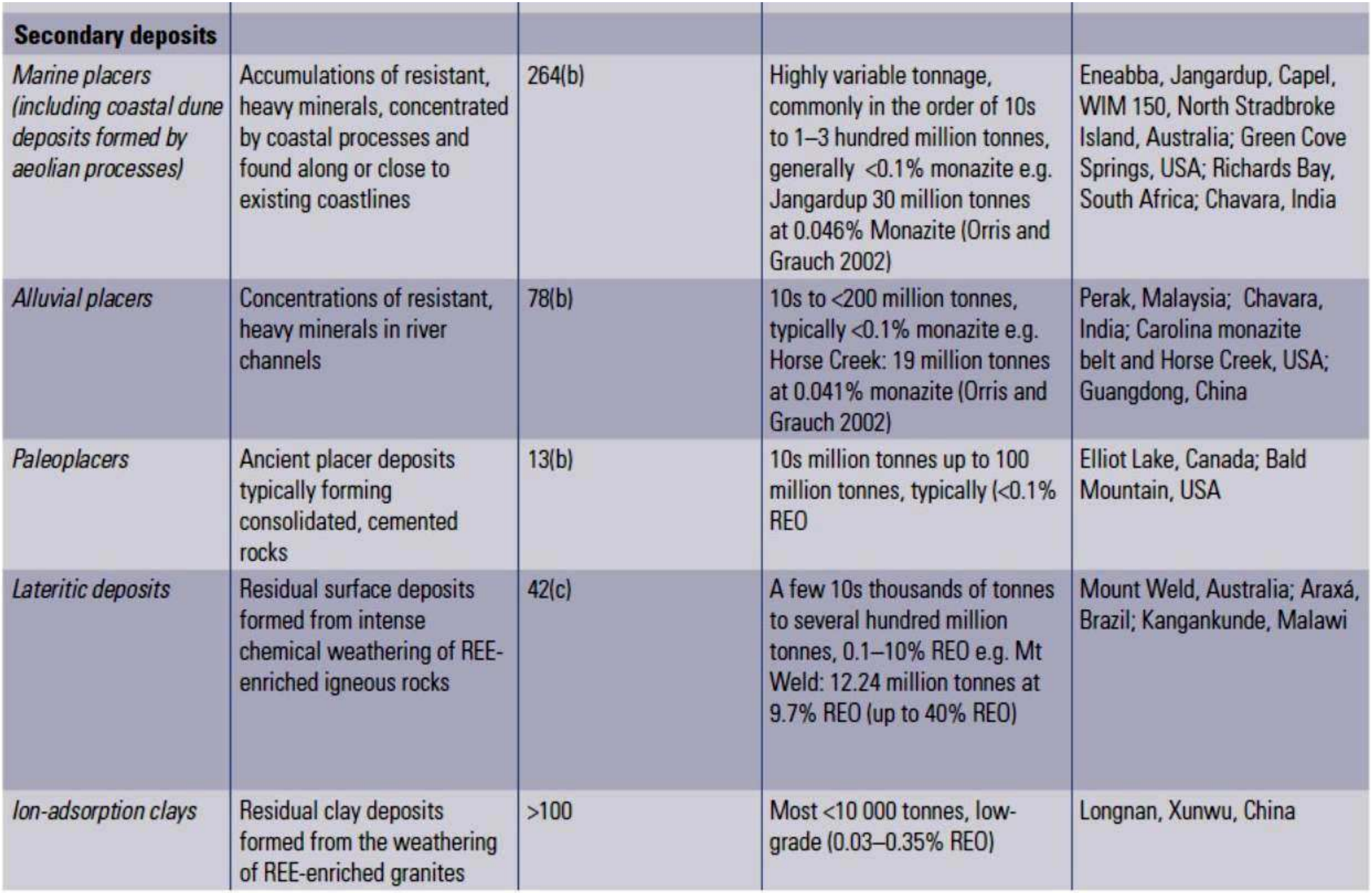
Exclusively **monazite**, as a by-product of **coastal sands** rich in Ti minerals (ilmenite and rutile) and zircon, e.g. Australia, Southern India, Ceylon, south-eastern coast of China, South Africa, Mozambique, Espirito Santo State in Brazil, the eastern USA coast and Madagascar or alluvial cassiterite deposits (Malesia).

- *meteoric alteration – supergene enrichment: residual, lateritic*

Particularly rich in REE are the lateritic horizons that are formed over the carbonatites in tropical – equatorial climates.

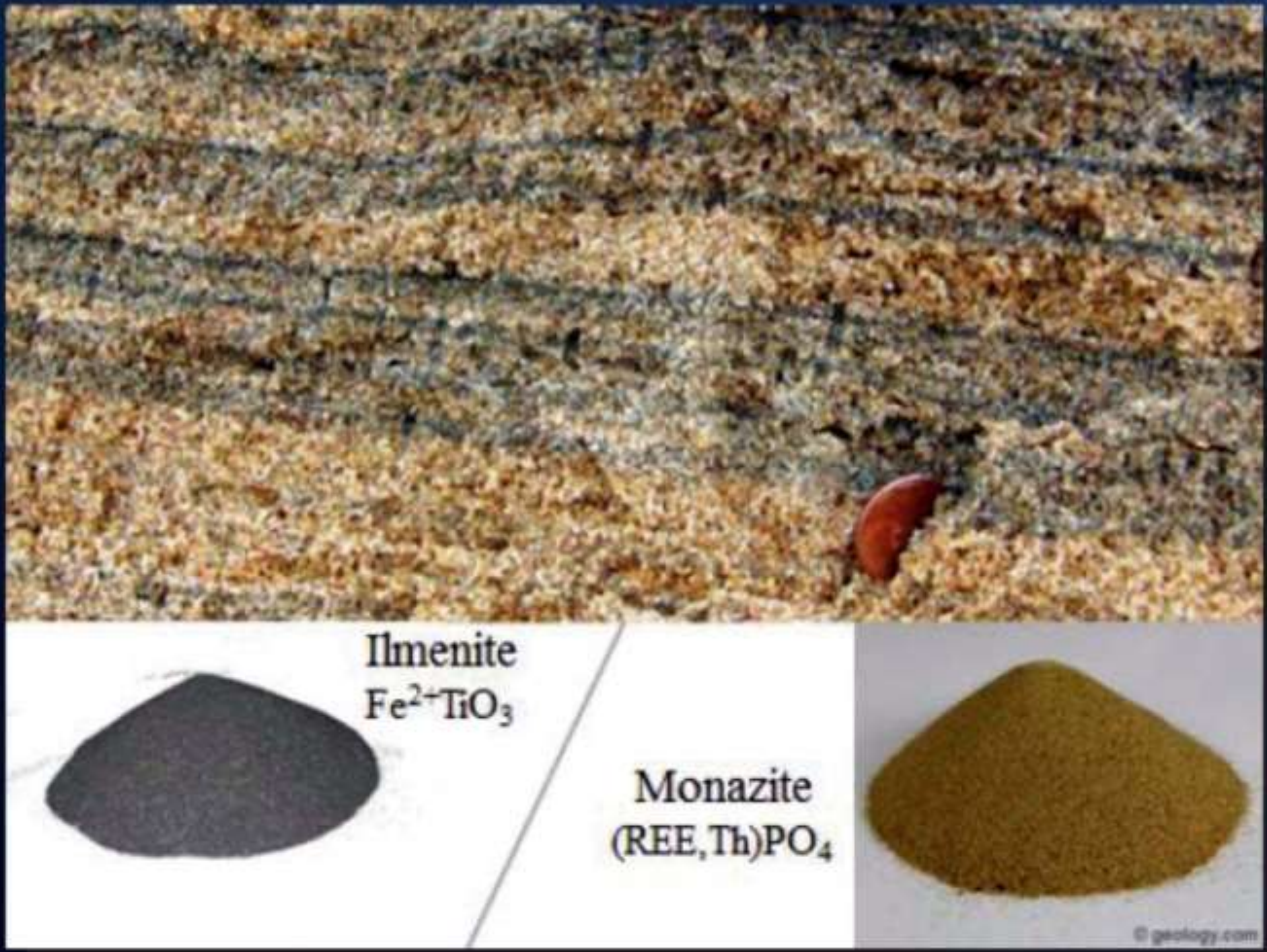
REE deposits in laterites may become the major REE source of the World.

Secondary ore deposits



Secondary deposits				
Marine placers (including coastal dune deposits formed by aeolian processes)	Accumulations of resistant, heavy minerals, concentrated by coastal processes and found along or close to existing coastlines	264(b)	Highly variable tonnage, commonly in the order of 10s to 1–3 hundred million tonnes, generally <0.1% monazite e.g. Jangardup 30 million tonnes at 0.046% Monazite (Orris and Grauch 2002)	Eneabba, Jangardup, Capel, WIM 150, North Stradbroke Island, Australia; Green Cove Springs, USA; Richards Bay, South Africa; Chavara, India
Alluvial placers	Concentrations of resistant, heavy minerals in river channels	78(b)	10s to <200 million tonnes, typically <0.1% monazite e.g. Horse Creek: 19 million tonnes at 0.041% monazite (Orris and Grauch 2002)	Perak, Malaysia; Chavara, India; Carolina monazite belt and Horse Creek, USA; Guangdong, China
Paleoplacers	Ancient placer deposits typically forming consolidated, cemented rocks	13(b)	10s million tonnes up to 100 million tonnes, typically (<0.1% REO	Elliot Lake, Canada; Bald Mountain, USA
Lateritic deposits	Residual surface deposits formed from intense chemical weathering of REE-enriched igneous rocks	42(c)	A few 10s thousands of tonnes to several hundred million tonnes, 0.1–10% REO e.g. Mt Weld: 12.24 million tonnes at 9.7% REO (up to 40% REO)	Mount Weld, Australia; Araxá, Brazil; Kangankunde, Malawi
Ion-adsorption clays	Residual clay deposits formed from the weathering of REE-enriched granites	>100	Most <10 000 tonnes, low-grade (0.03–0.35% REO)	Longnan, Xunwu, China

Monazite-bearing Stream and Beach Placer Deposits



Carbonatites vs. ion-adsorption ores

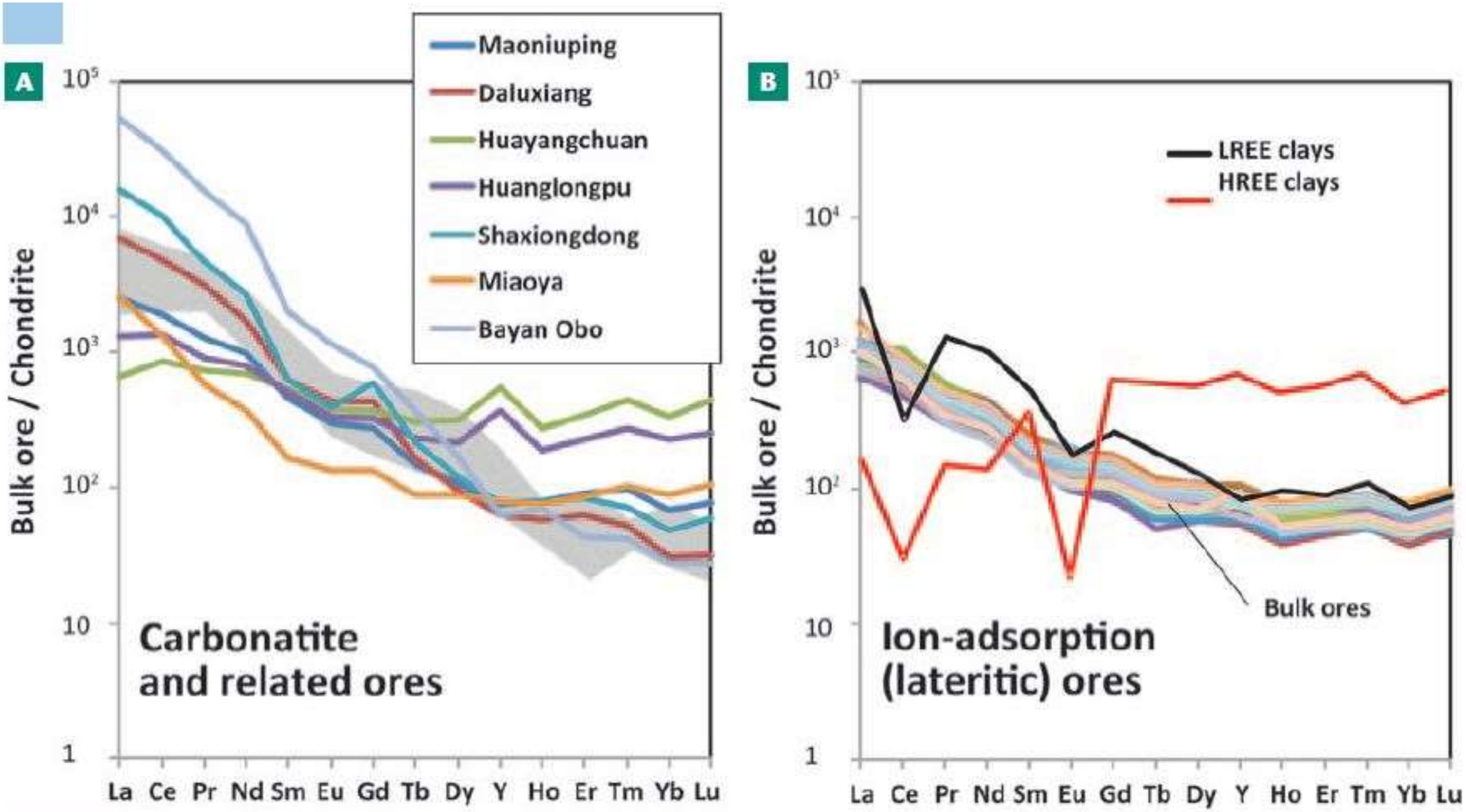


FIGURE 2 Representative chondrite-normalized plots showing the distribution of REEs in the deposits discussed in the text. Yttrium is plotted as a pseudo-lanthanide between Dy and Ho. (**A**) Bulk-rock composition of carbonatites and related ores. The grey field shows the global range for carbonatites, from Woolley and Kempe (1989). (**B**) Bulk-rock and mineralogical composition of ion-adsorption (lateritic) ores

REE deposits of China

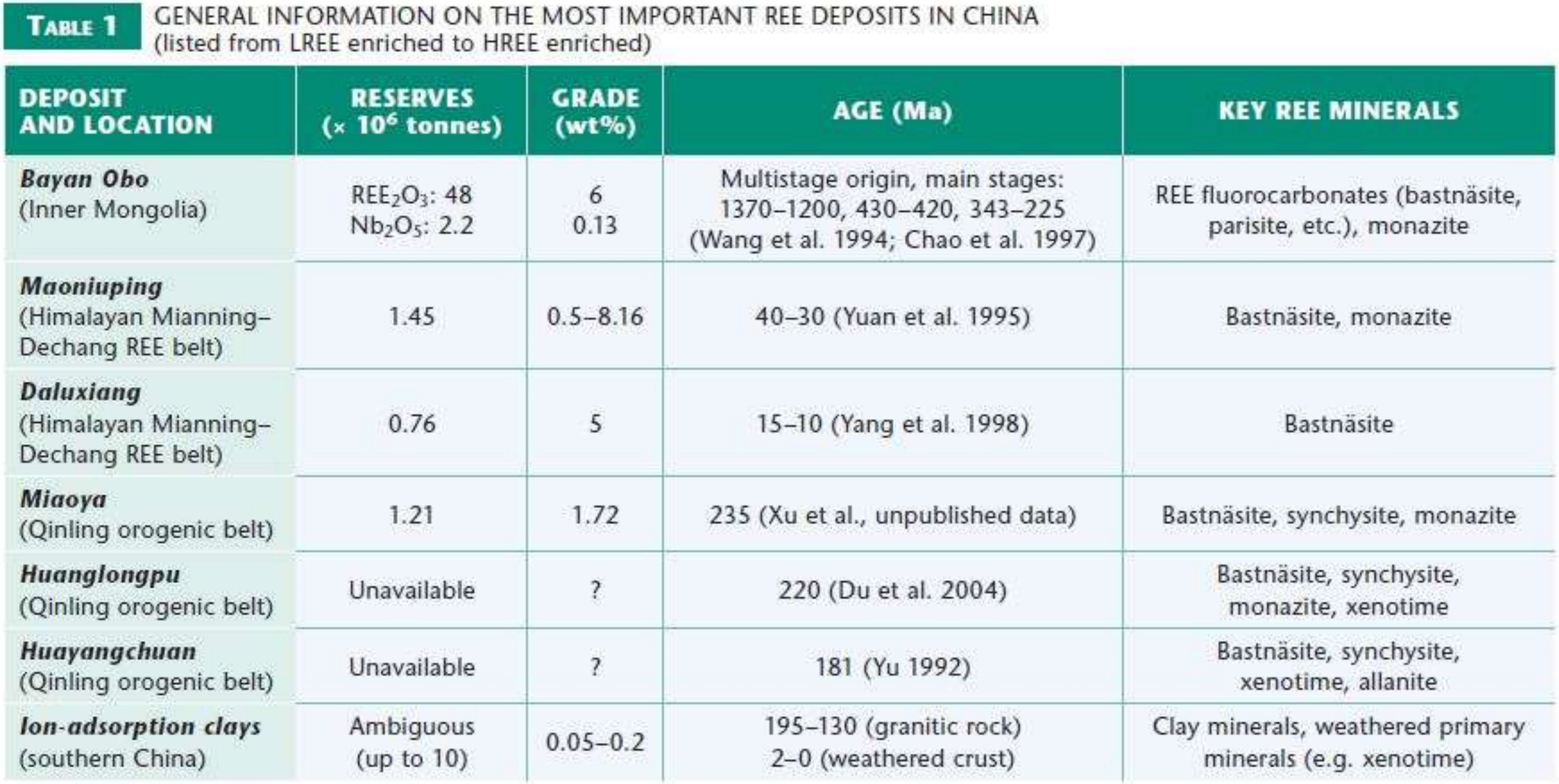


TABLE 1 GENERAL INFORMATION ON THE MOST IMPORTANT REE DEPOSITS IN CHINA (listed from LREE enriched to HREE enriched)

DEPOSIT AND LOCATION	RESERVES (× 10^6 tonnes)	GRADE (wt%)	AGE (Ma)	KEY REE MINERALS
Bayan Obo (Inner Mongolia)	REE_2O_3: 48 Nb_2O_5: 2.2	6 0.13	Multistage origin, main stages: 1370–1200, 430–420, 343–225 (Wang et al. 1994; Chao et al. 1997)	REE fluorocarbonates (bastnäsite, parisite, etc.), monazite
Maoniuping (Himalayan Mianning–Dechang REE belt)	1.45	0.5–8.16	40–30 (Yuan et al. 1995)	Bastnäsite, monazite
Daluxiang (Himalayan Mianning–Dechang REE belt)	0.76	5	15–10 (Yang et al. 1998)	Bastnäsite
Miaoya (Qinling orogenic belt)	1.21	1.72	235 (Xu et al., unpublished data)	Bastnäsite, synchysite, monazite
Huanglongpu (Qinling orogenic belt)	Unavailable	?	220 (Du et al. 2004)	Bastnäsite, synchysite, monazite, xenotime
Huayangchuan (Qinling orogenic belt)	Unavailable	?	181 (Yu 1992)	Bastnäsite, synchysite, xenotime, allanite
Ion-adsorption clays (southern China)	Ambiguous (up to 10)	0.05–0.2	195–130 (granitic rock) 2–0 (weathered crust)	Clay minerals, weathered primary minerals (e.g. xenotime)

REE mines and advanced projects

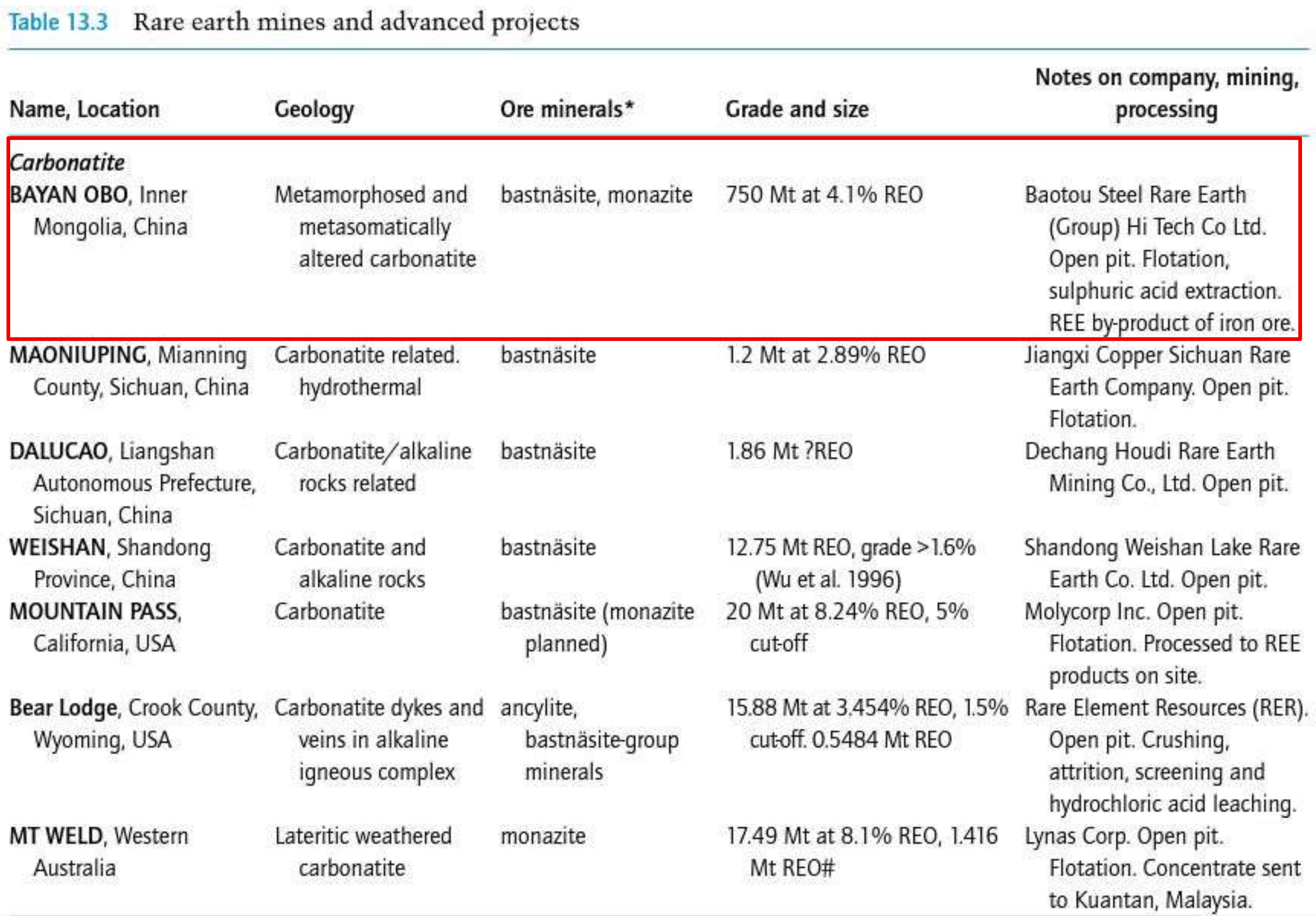


Table 13.3 Rare earth mines and advanced projects

Name, Location	Geology	Ore minerals*	Grade and size	Notes on company, mining, processing
Carbonatite				
BAYAN OBO, Inner Mongolia, China	Metamorphosed and metasomatically altered carbonatite	bastnäsite, monazite	750 Mt at 4.1% REO	Baotou Steel Rare Earth (Group) Hi Tech Co Ltd. Open pit. Flotation, sulphuric acid extraction. REE by-product of iron ore.
MAONIUPING, Mianning County, Sichuan, China	Carbonatite related. hydrothermal	bastnäsite	1.2 Mt at 2.89% REO	Jiangxi Copper Sichuan Rare Earth Company. Open pit. Flotation.
DALUCAO, Liangshan Autonomous Prefecture, Sichuan, China	Carbonatite/alkaline rocks related	bastnäsite	1.86 Mt ?REO	Dechang Houdi Rare Earth Mining Co., Ltd. Open pit.
WEISHAN, Shandong Province, China	Carbonatite and alkaline rocks	bastnäsite	12.75 Mt REO, grade >1.6% (Wu et al. 1996)	Shandong Weishan Lake Rare Earth Co. Ltd. Open pit.
MOUNTAIN PASS, California, USA	Carbonatite	bastnäsite (monazite planned)	20 Mt at 8.24% REO, 5% cut-off	Molycorp Inc. Open pit. Flotation. Processed to REE products on site.
Bear Lodge, Crook County, Wyoming, USA	Carbonatite dykes and veins in alkaline igneous complex	ancylite, bastnäsite-group minerals	15.88 Mt at 3.454% REO, 1.5% cut-off. 0.5484 Mt REO	Rare Element Resources (RER). Open pit. Crushing, attrition, screening and hydrochloric acid leaching.
MT WELD, Western Australia	Lateritic weathered carbonatite	monazite	17.49 Mt at 8.1% REO, 1.416 Mt REO#	Lynas Corp. Open pit. Flotation. Concentrate sent to Kuantan, Malaysia.

REE mines and advanced projects

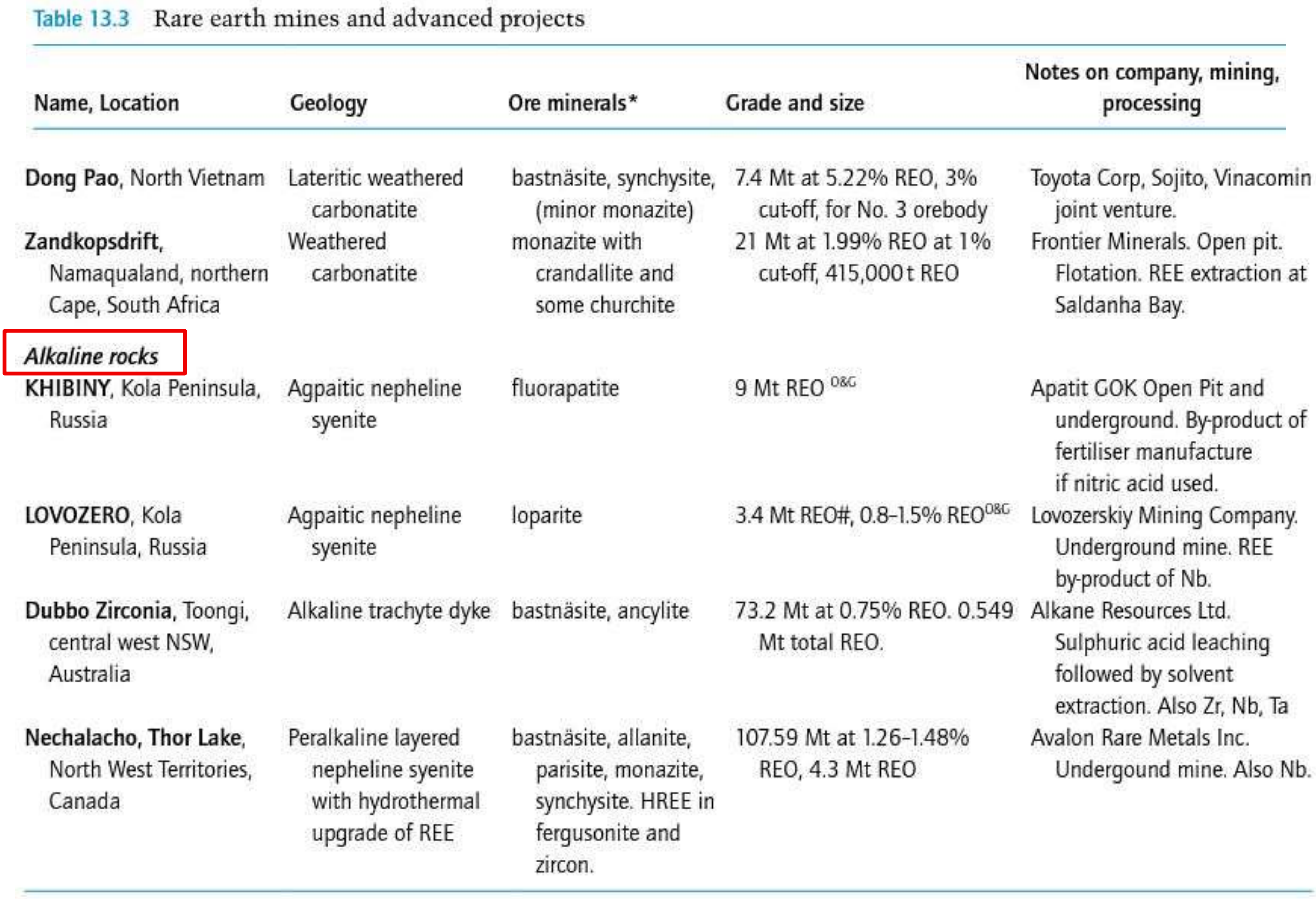


Table 13.3 Rare earth mines and advanced projects

Name, Location	Geology	Ore minerals*	Grade and size	Notes on company, mining, processing
Dong Pao, North Vietnam	Lateritic weathered carbonatite	bastnäsite, synchysite, (minor monazite)	7.4 Mt at 5.22% REO, 3% cut-off, for No. 3 orebody	Toyota Corp, Sojito, Vinacomin joint venture.
Zandkopsdrift, Namaqualand, northern Cape, South Africa	Weathered carbonatite	monazite with crandallite and some churchite	21 Mt at 1.99% REO at 1% cut-off, 415,000 t REO	Frontier Minerals. Open pit. Flotation. REE extraction at Saldanha Bay.
Alkaline rocks				
KHIBINY, Kola Peninsula, Russia	Agpaitic nepheline syenite	fluorapatite	9 Mt REO $^{O\&G}$	Apatit GOK Open Pit and underground. By-product of fertiliser manufacture if nitric acid used.
LOVOZERO, Kola Peninsula, Russia	Agpaitic nepheline syenite	loparite	3.4 Mt REO#, 0.8–1.5% REO$^{O\&G}$	Lovozerskiy Mining Company. Underground mine. REE by-product of Nb.
Dubbo Zirconia, Toongi, central west NSW, Australia	Alkaline trachyte dyke	bastnäsite, ancylite	73.2 Mt at 0.75% REO. 0.549 Mt total REO.	Alkane Resources Ltd. Sulphuric acid leaching followed by solvent extraction. Also Zr, Nb, Ta
Nechalacho, Thor Lake, North West Territories, Canada	Peralkaline layered nepheline syenite with hydrothermal upgrade of REE	bastnäsite, allanite, parisite, monazite, synchysite. HREE in fergusonite and zircon.	107.59 Mt at 1.26–1.48% REO, 4.3 Mt REO	Avalon Rare Metals Inc. Undergound mine. Also Nb.

REE mines and advanced projects

Name, Location	Geology	Ore minerals*	Grade and size	Notes on company, mining, processing
Kvanefjeld, Ilimaussaq Gardar Province, Greenland	Agpaitic nepheline syenite	steenstrupine, (eudialyte)	619 Mt at 10,585 ppm REO, 6.55 Mt REO	Greenland Minerals and Energy Ltd and Westrip Holdings. Open pit. Carbonate pressure leaching to recover U, precipitation of REE.
Strange Lake, NE Quebec/NW Labrador border, Canada	Peralkaline granite (hypersolvus, subsolvus and pegmatite) with additional hydrothermal concentration of REE	yttropyrochlore, kainosite, allanite, gadolinite, gerenite, keiviite: (fluorocarbonates & monazite)	114.8 Mt at 0.999 % REO, 43% HREE	Quest Rare Metals.
Zeus, Kipawa alkaline complex, Témiscamingue, Quebec, Canada	Alkaline compex with syenite and granite	eudialyte, Y-bearing titanite, britholite	67,200 t REO, significant HREE	Matamec Explorations. Open pit. Mild crushing and leaching. Also Zr.
Kutessay II, Aktyuz Ore field, Chu Oblast, Kyrgyz Republic	3 mineralised zones, (I, II, III). Massive pockets of REE carbonates	monazite, xenotime-(Y), bastnäsite-(Y), parisite- (Y)?, synchysite-(Y), yttrofluorite, fluorcerite	16.27 Mt at 0.264% REO^{BGS} 50:50 LREE:HREE	Stans Energy Corp. Former REE mine. Produced all 15 REE.

REE mines and advanced projects

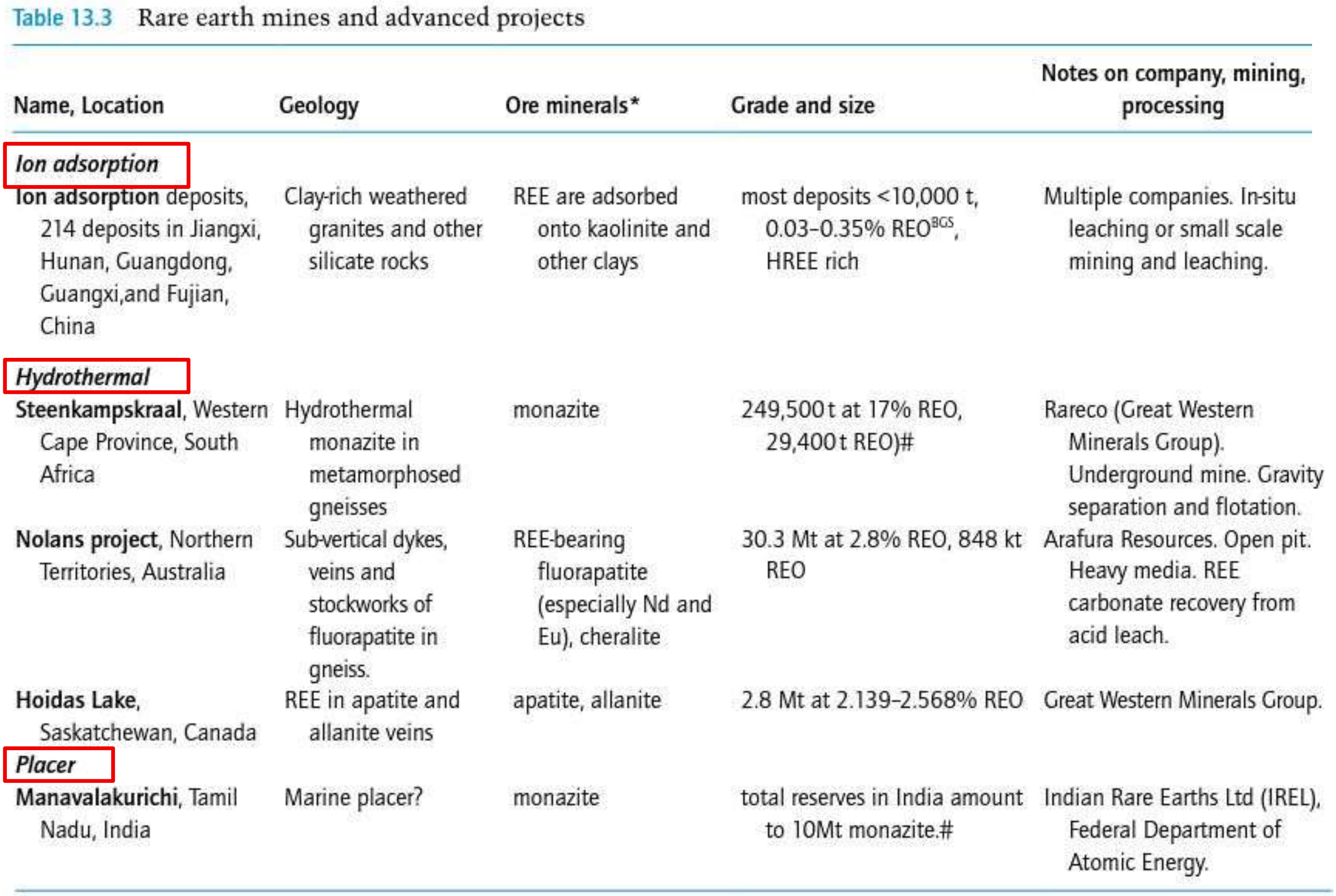
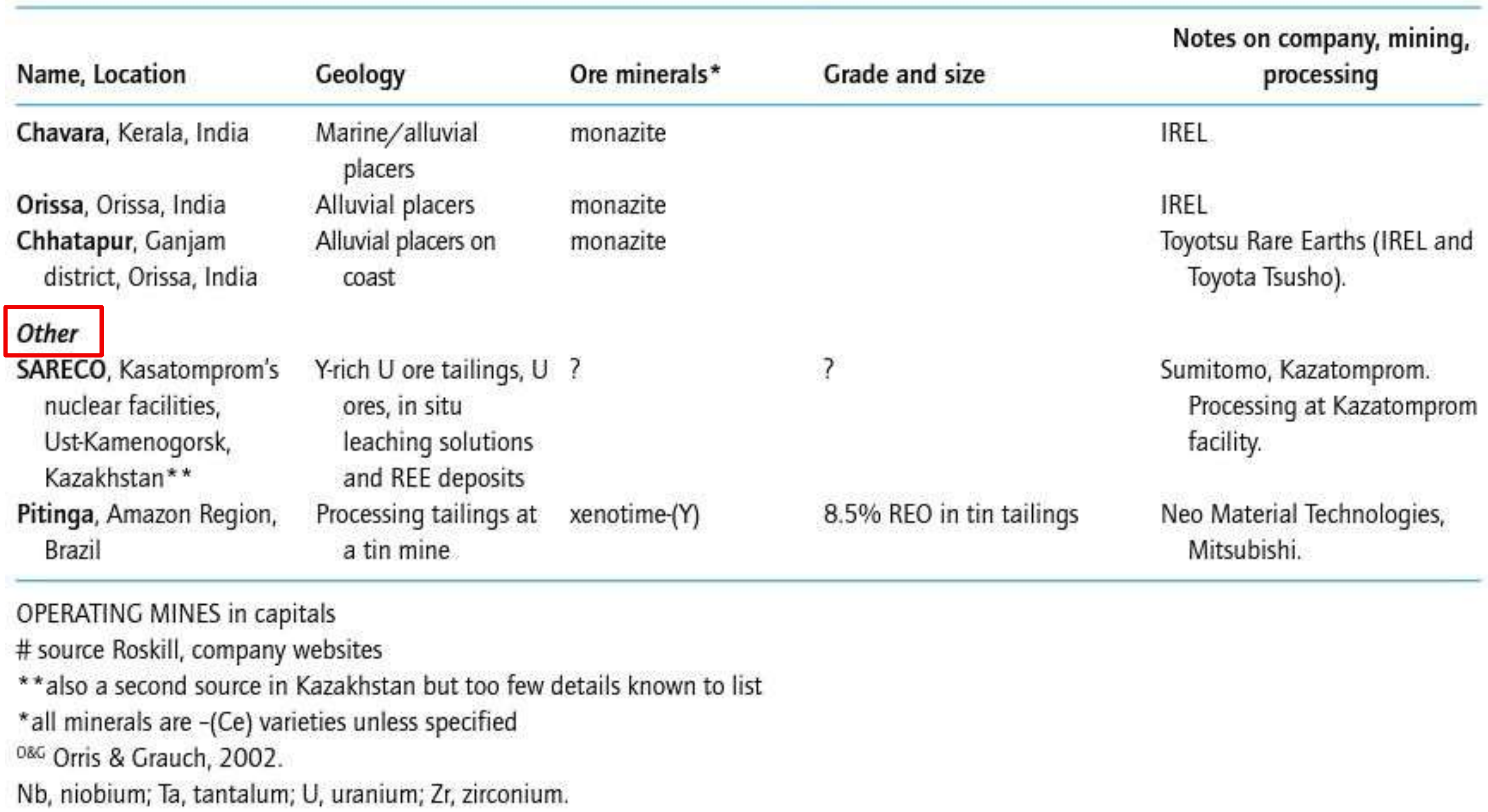


Table 13.3 Rare earth mines and advanced projects

Name, Location	Geology	Ore minerals*	Grade and size	Notes on company, mining, processing
Ion adsorption				
Ion adsorption deposits, 214 deposits in Jiangxi, Hunan, Guangdong, Guangxi,and Fujian, China	Clay-rich weathered granites and other silicate rocks	REE are adsorbed onto kaolinite and other clays	most deposits <10,000 t, 0.03–0.35% REO^{BGS}, HREE rich	Multiple companies. In-situ leaching or small scale mining and leaching.
Hydrothermal				
Steenkampskraal, Western Cape Province, South Africa	Hydrothermal monazite in metamorphosed gneisses	monazite	249,500 t at 17% REO, 29,400 t REO)#	Rareco (Great Western Minerals Group). Underground mine. Gravity separation and flotation.
Nolans project, Northern Territories, Australia	Sub-vertical dykes, veins and stockworks of fluorapatite in gneiss.	REE-bearing fluorapatite (especially Nd and Eu), cheralite	30.3 Mt at 2.8% REO, 848 kt REO	Arafura Resources. Open pit. Heavy media. REE carbonate recovery from acid leach.
Hoidas Lake, Saskatchewan, Canada	REE in apatite and allanite veins	apatite, allanite	2.8 Mt at 2.139–2.568% REO	Great Western Minerals Group.
Placer				
Manavalakurichi, Tamil Nadu, India	Marine placer?	monazite	total reserves in India amount to 10Mt monazite.#	Indian Rare Earths Ltd (IREL), Federal Department of Atomic Energy.

REE mines and advanced projects



Name, Location	Geology	Ore minerals*	Grade and size	Notes on company, mining, processing
Chavara, Kerala, India	Marine/alluvial placers	monazite		IREL
Orissa, Orissa, India	Alluvial placers	monazite		IREL
Chhatapur, Ganjam district, Orissa, India	Alluvial placers on coast	monazite		Toyotsu Rare Earths (IREL and Toyota Tsusho).
Other				
SARECO, Kasatomprom's nuclear facilities, Ust-Kamenogorsk, Kazakhstan**	Y-rich U ore tailings, U ores, in situ leaching solutions and REE deposits	?	?	Sumitomo, Kazatomprom. Processing at Kazatomprom facility.
Pitinga, Amazon Region, Brazil	Processing tailings at a tin mine	xenotime-(Y)	8.5% REO in tin tailings	Neo Material Technologies, Mitsubishi.

OPERATING MINES in capitals

source Roskill, company websites

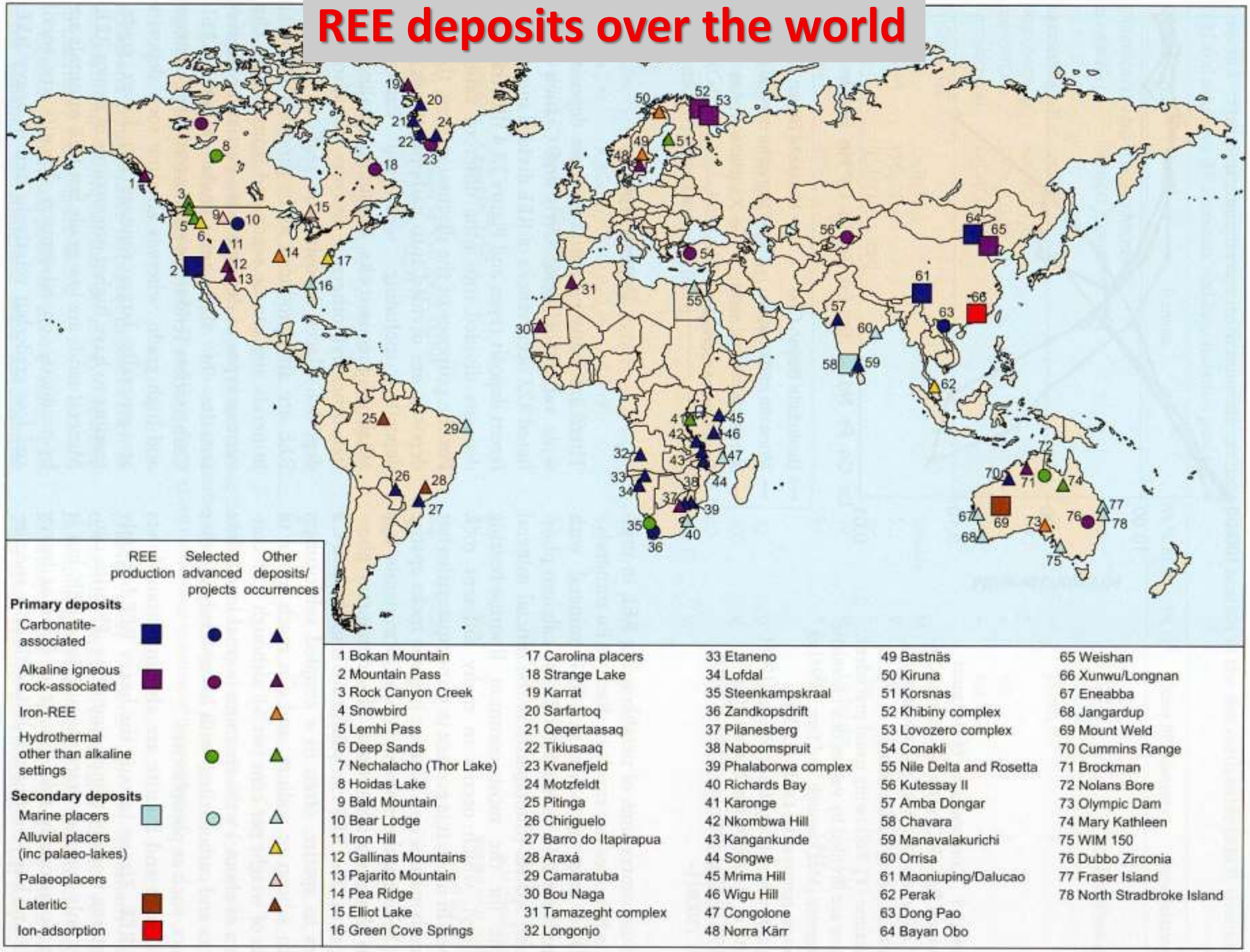
**also a second source in Kazakhstan but too few details known to list

*all minerals are –(Ce) varieties unless specified

O&G Orris & Grauch, 2002.

Nb, niobium; Ta, tantalum; U, uranium; Zr, zirconium.

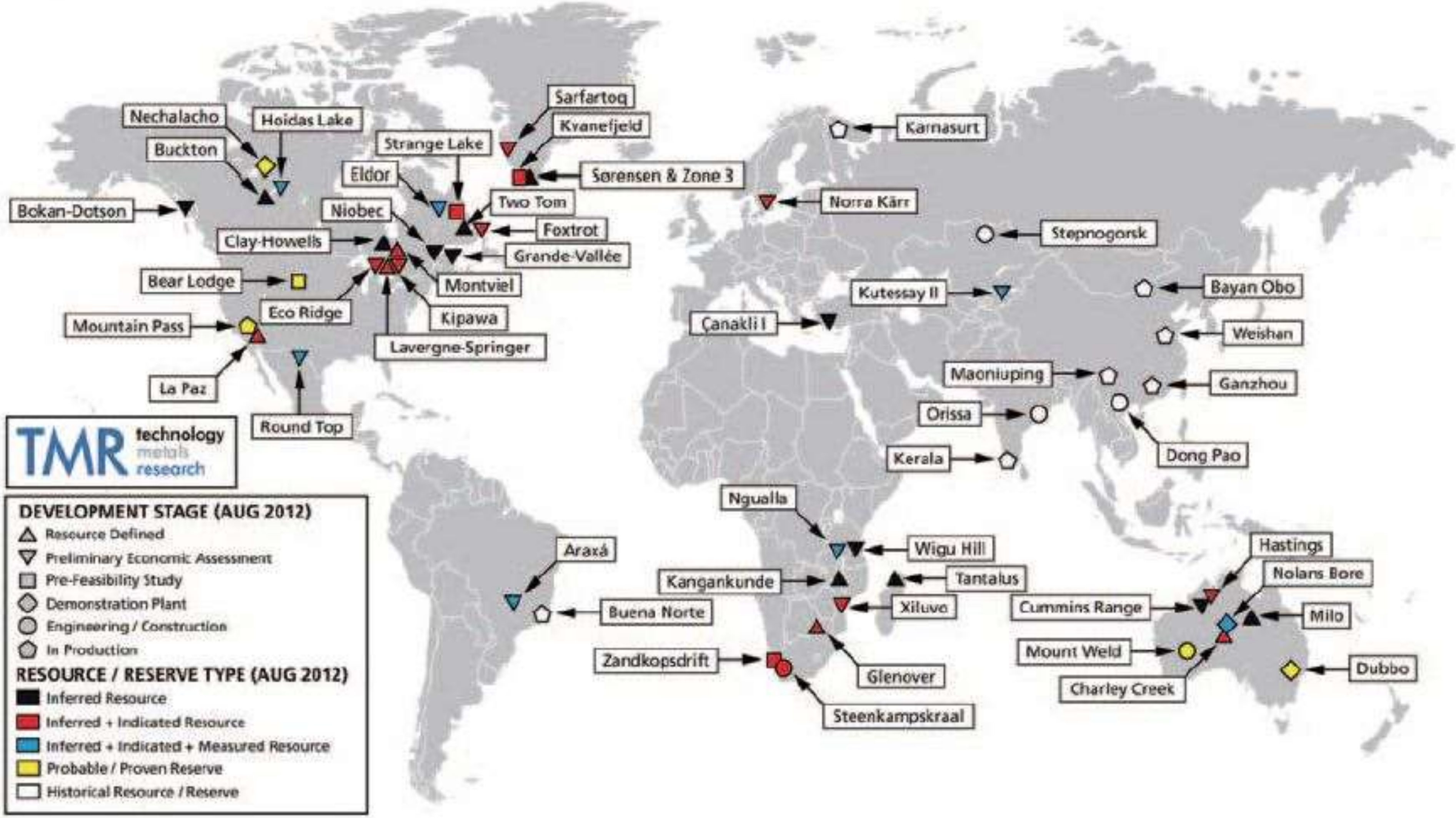
REE deposits over the world



	REE production	Selected advanced projects	Other deposits/ occurrences
Primary deposits			
Carbonatite-associated	■	●	▲
Alkaline igneous rock-associated	■	●	▲
Iron-REE			▲
Hydrothermal other than alkaline settings		●	▲
Secondary deposits			
Marine placers	□	○	△
Alluvial placers (inc palaeo-lakes)			△
Palaeoplacers			△
Lateritic	■		▲
Ion-adsorption	■		

1 Bokan Mountain
2 Mountain Pass
3 Rock Canyon Creek
4 Snowbird
5 Lemhi Pass
6 Deep Sands
7 Nechalacho (Thor Lake)
8 Hoidas Lake
9 Bald Mountain
10 Bear Lodge
11 Iron Hill
12 Gallinas Mountains
13 Pajarito Mountain
14 Pea Ridge
15 Elliot Lake
16 Green Cove Springs
17 Carolina placers
18 Strange Lake
19 Karrat
20 Sarfartoq
21 Qeqertaasaq
22 Tikiusaaq
23 Kvanefjeld
24 Motzfeldt
25 Pitinga
26 Chiriguelo
27 Barro do Itapirapua
28 Araxá
29 Camaratuba
30 Bou Naga
31 Tamazeght complex
32 Longonjo
33 Etaneno
34 Lofdal
35 Steenkampskraal
36 Zandkopsdrift
37 Pilanesberg
38 Naboomspruit
39 Phalaborwa complex
40 Richards Bay
41 Karonge
42 Nkombwa Hill
43 Kangankunde
44 Songwe
45 Mrima Hill
46 Wigu Hill
47 Congolone
48 Norra Kärr
49 Bastnäs
50 Kiruna
51 Korsnas
52 Khibiny complex
53 Lovozero complex
54 Conakli
55 Nile Delta and Rosetta
56 Kutessay II
57 Amba Dongar
58 Chavara
59 Manavalakurichi
60 Orrisa
61 Maoniuping/Dalucao
62 Perak
63 Dong Pao
64 Bayan Obo
65 Weishan
66 Xunwu/Longnan
67 Eneabba
68 Jangardup
69 Mount Weld
70 Cummins Range
71 Brockman
72 Nolans Bore
73 Olympic Dam
74 Mary Kathleen
75 WIM 150
76 Dubbo Zirconia
77 Fraser Island
78 North Stradbroke Island

REE advanced projects



REE reserves – size and grade

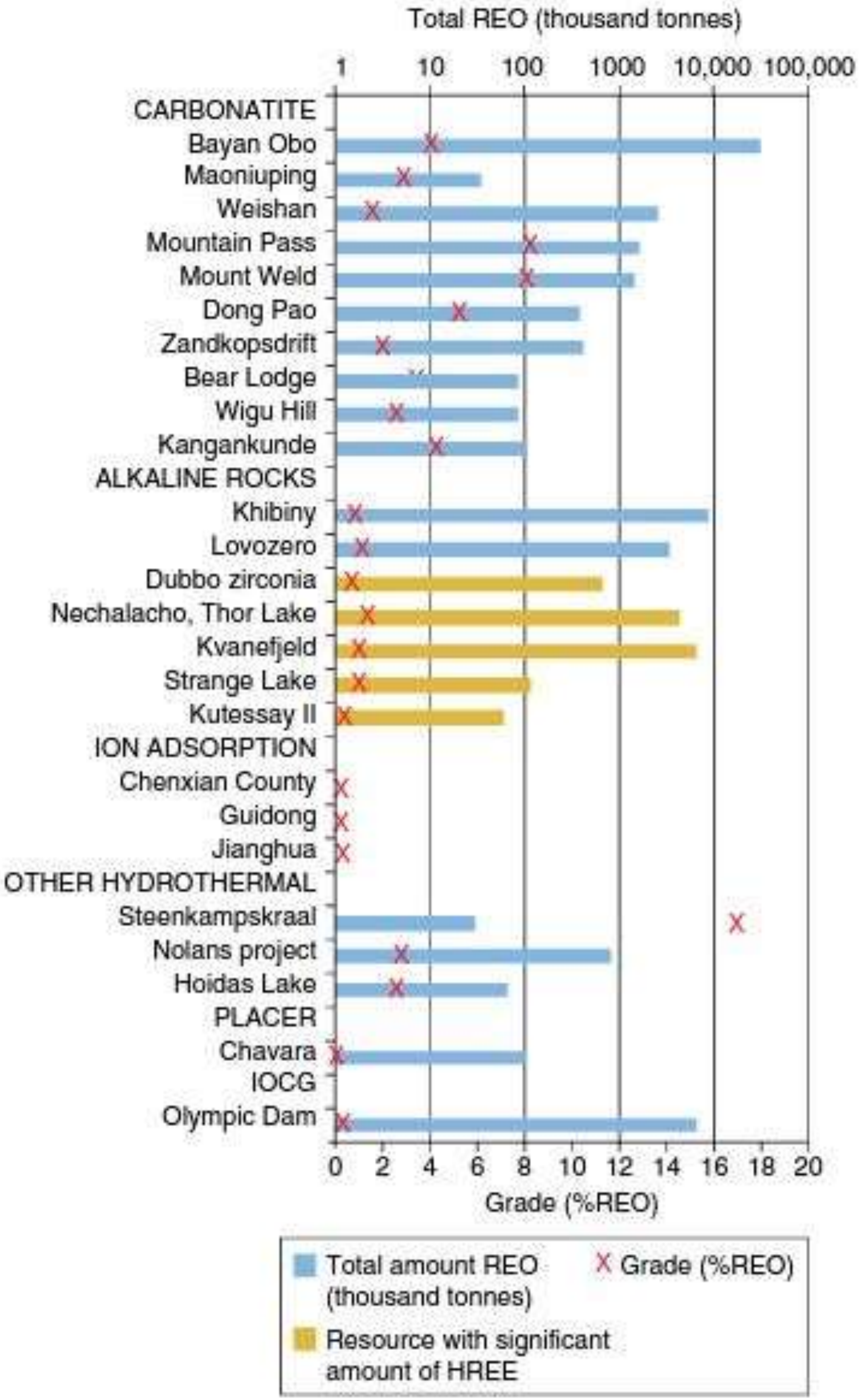


Figure 13.5 Comparison of the size and grade of rare earth mines and advanced development projects. (Data from Table 13.3.)

REO world reserves

Country	Reserves (tonnes)
China	50 000 000
Commonwealth of Independent States	19 000 000
United States of America	13 000 000
India	3 100 000
Australia	1 600 000
Other Countries	22 100 000
World Total	**113 800 000**

Table Estimated world REO reserves (reserves are defined by USGS as that part of the reserve base which could be economically extracted or produced at the time of determination. The term reserves need not signify that extraction facilities are in place and operative. Reserves include only recoverable materials (Cordier, 2011).

REE: ENVIRONMENTAL ISSUES

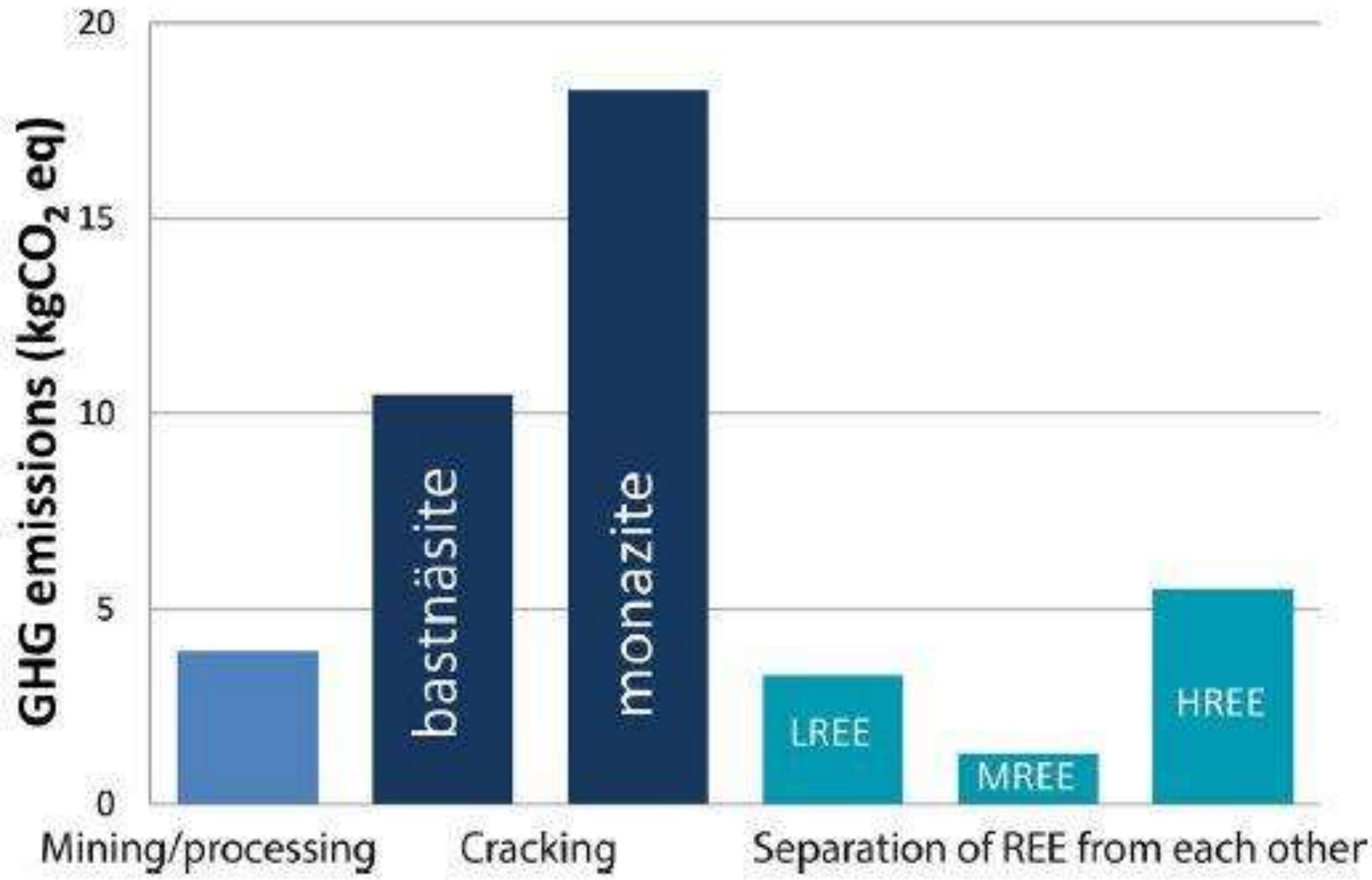
The extraction and processing of REE has a **strong environmental impact**:

- the presence of **radioactive contamination** for some REM, such as xenotime and monazite (may contain significant amounts of U and Th);
- **HF and H_2SO_4 containing gases** are released in the environment, as well as **acid waters** and **solid radioactive waste**;
- REE production requires **large quantities of electricity** (even though the same REE are used for technologies related to **renewable energies**).

REE: ENVIRONMENTAL ISSUES - Baotou (China)

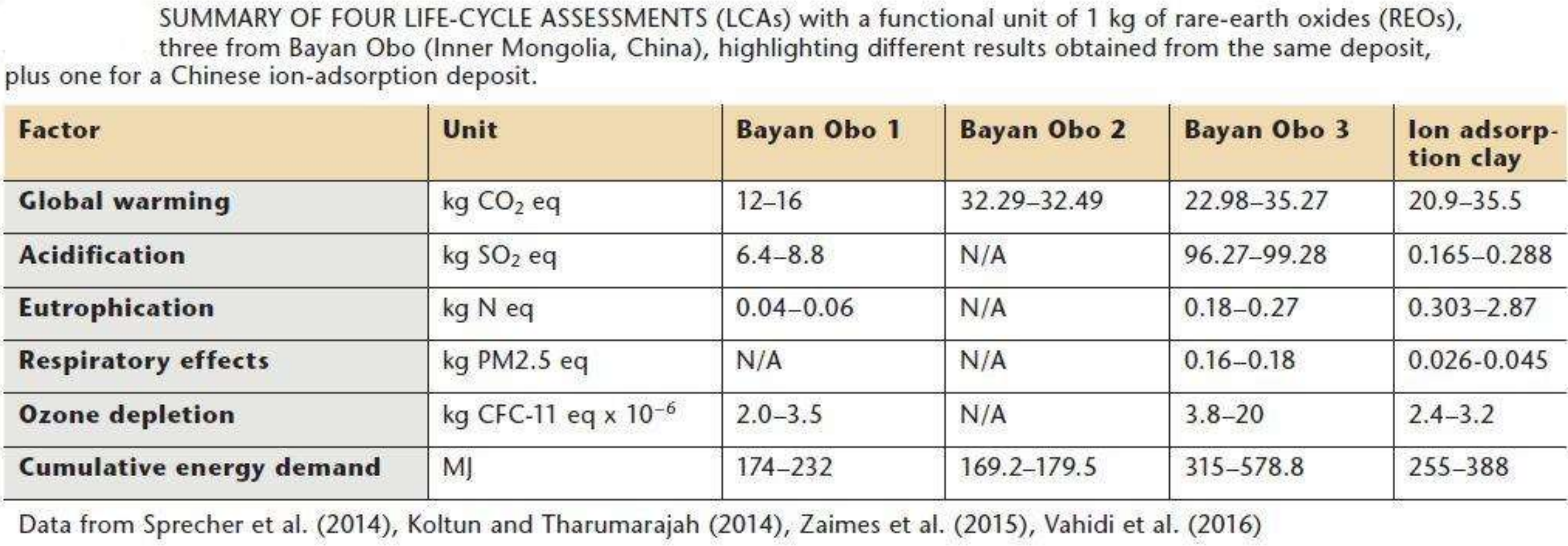
REE: ENVIRONMENTAL ISSUES - Baotou (China)

REE: GREENHOUSE GAS (GHG) EMISSIONS



Greenhouse gas (GHG) emissions equivalent per kg of rare-earth oxide produced calculated from a life cycle assessment of a) mining, concentrating Bayan Obo REE ore; b) dissolving (cracking) the two ore minerals bastnäsite and monazite to release their REEs; c) separating the light (L), medium (M) and heavy (H) REEs from each other. After Koltun and Tharumarajah (2014).

REE: LIFE-CYCLE ASSESSMENTS (LCAs)

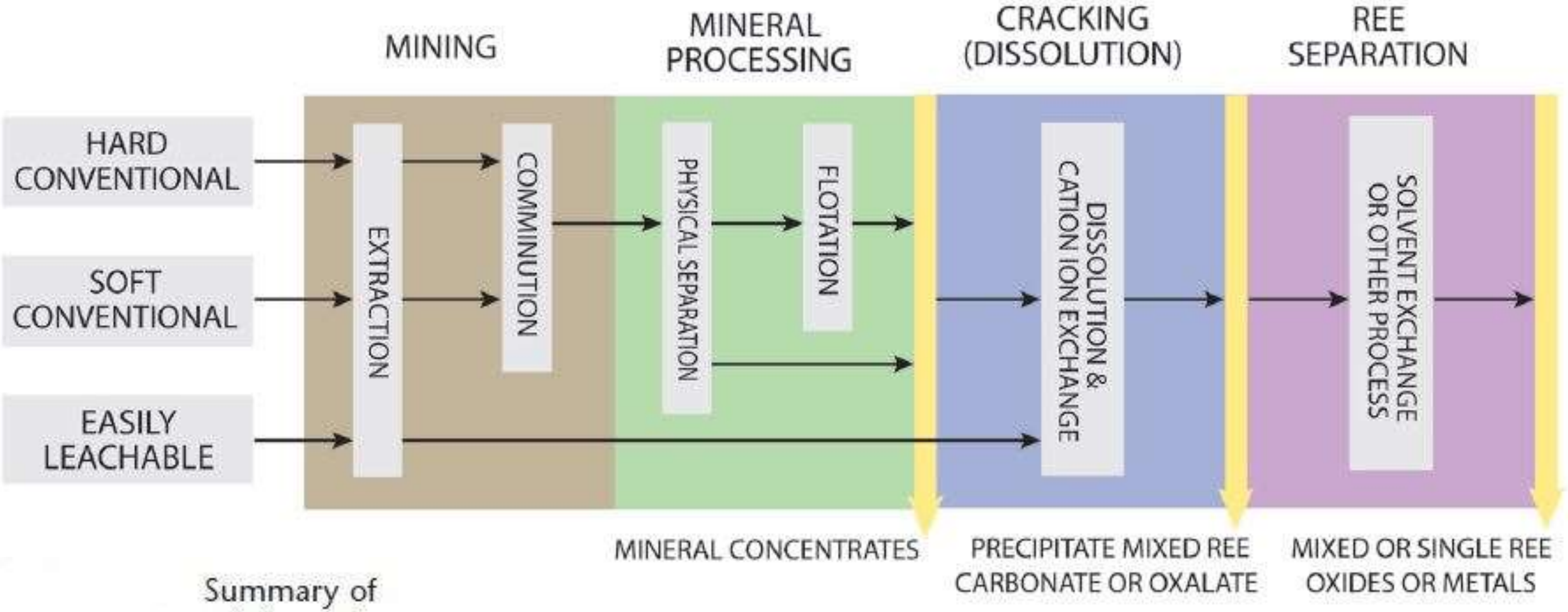


SUMMARY OF FOUR LIFE-CYCLE ASSESSMENTS (LCAs) with a functional unit of 1 kg of rare-earth oxides (REOs), three from Bayan Obo (Inner Mongolia, China), highlighting different results obtained from the same deposit, plus one for a Chinese ion-adsorption deposit.

Factor	Unit	Bayan Obo 1	Bayan Obo 2	Bayan Obo 3	Ion adsorption clay
Global warming	kg CO_2 eq	12–16	32.29–32.49	22.98–35.27	20.9–35.5
Acidification	kg SO_2 eq	6.4–8.8	N/A	96.27–99.28	0.165–0.288
Eutrophication	kg N eq	0.04–0.06	N/A	0.18–0.27	0.303–2.87
Respiratory effects	kg PM2.5 eq	N/A	N/A	0.16–0.18	0.026-0.045
Ozone depletion	kg CFC-11 eq x 10^{-6}	2.0–3.5	N/A	3.8–20	2.4–3.2
Cumulative energy demand	MJ	174–232	169.2–179.5	315–578.8	255–388

Data from Sprecher et al. (2014), Koltun and Tharumarajah (2014), Zaimes et al. (2015), Vahidi et al. (2016)

REE: MINING AND PROCESSING ROUTES



MINING

MINERAL PROCESSING

CRACKING (DISSOLUTION)

REE SEPARATION

HARD CONVENTIONAL

SOFT CONVENTIONAL

EASILY LEACHABLE

EXTRACTION

COMMINUTION

PHYSICAL SEPARATION

FLOTATION

DISSOLUTION & CATION ION EXCHANGE

SOLVENT EXCHANGE OR OTHER PROCESS

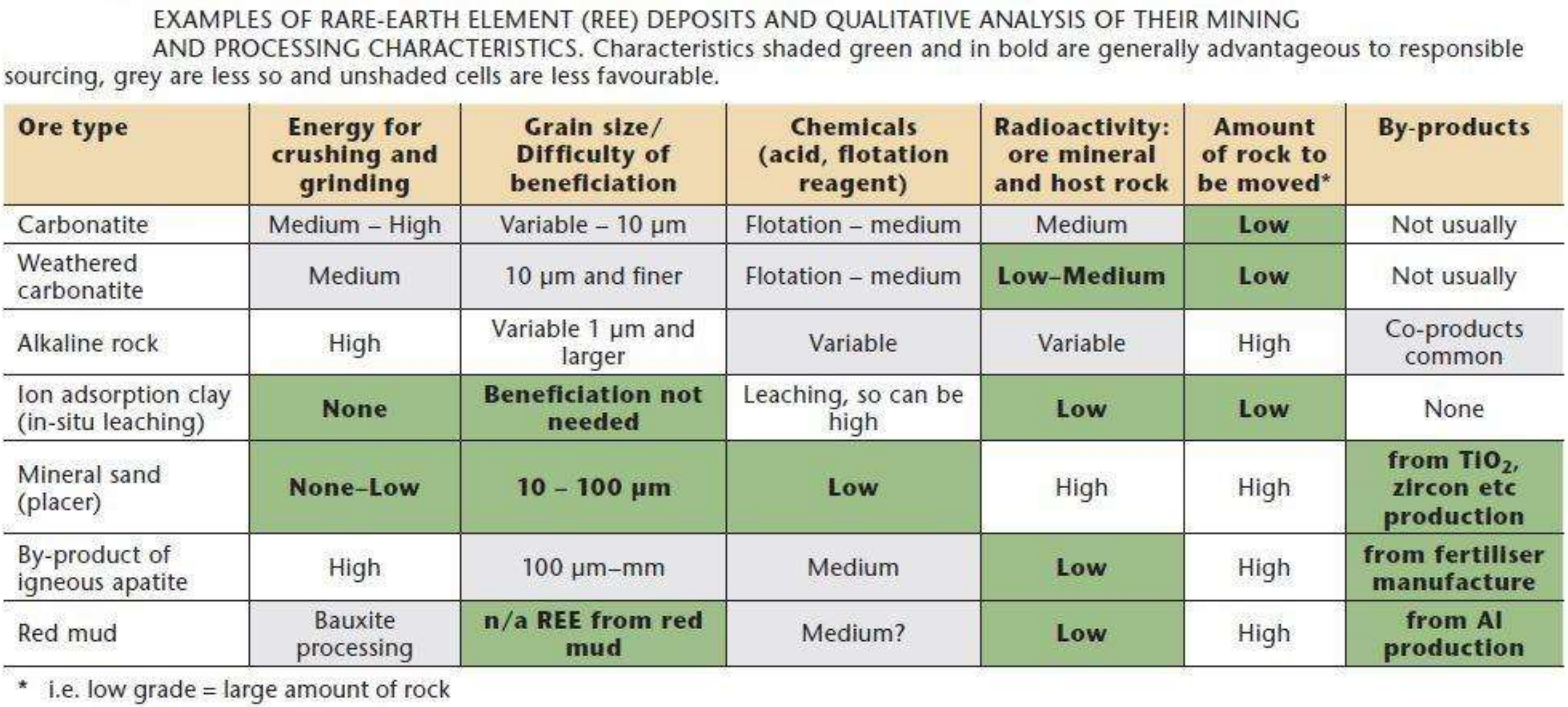
MINERAL CONCENTRATES

PRECIPITATE MIXED REE CARBONATE OR OXALATE

MIXED OR SINGLE REE OXIDES OR METALS

Summary of mining and processing routes for rare-earth element (REE) deposits. Ores are divided into three types: hard conventional, such as igneous carbonatite and alkaline igneous rocks; soft conventional, such as mineral sands; and easily leachable, which includes ion-adsorption clays.

REE: MINING AND PROCESSING ROUTES

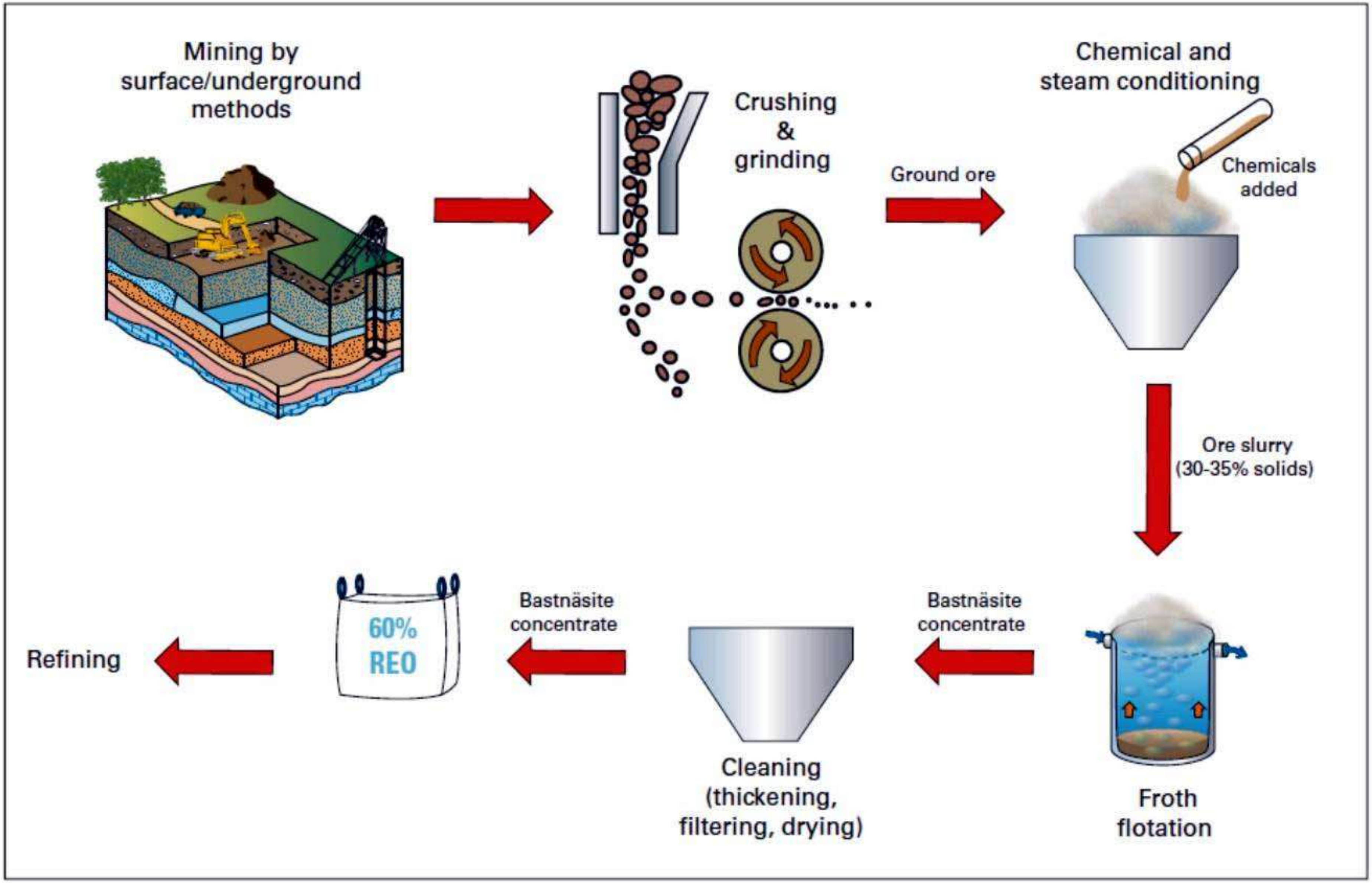


EXAMPLES OF RARE-EARTH ELEMENT (REE) DEPOSITS AND QUALITATIVE ANALYSIS OF THEIR MINING AND PROCESSING CHARACTERISTICS. Characteristics shaded green and in bold are generally advantageous to responsible sourcing, grey are less so and unshaded cells are less favourable.

Ore type	**Energy for crushing and grinding**	**Grain size/ Difficulty of beneficiation**	**Chemicals (acid, flotation reagent)**	**Radioactivity: ore mineral and host rock**	**Amount of rock to be moved***	**By-products**
Carbonatite	Medium – High	Variable – 10 µm	Flotation – medium	Medium	**Low**	Not usually
Weathered carbonatite	Medium	10 µm and finer	Flotation – medium	**Low–Medium**	**Low**	Not usually
Alkaline rock	High	Variable 1 µm and larger	Variable	Variable	High	Co-products common
Ion adsorption clay (in-situ leaching)	**None**	**Beneficiation not needed**	Leaching, so can be high	**Low**	**Low**	None
Mineral sand (placer)	**None–Low**	**10 – 100 µm**	**Low**	High	High	**from TiO_2, zircon etc production**
By-product of igneous apatite	High	100 µm–mm	Medium	**Low**	High	**from fertiliser manufacture**
Red mud	Bauxite processing	**n/a REE from red mud**	Medium?	**Low**	High	**from Al production**

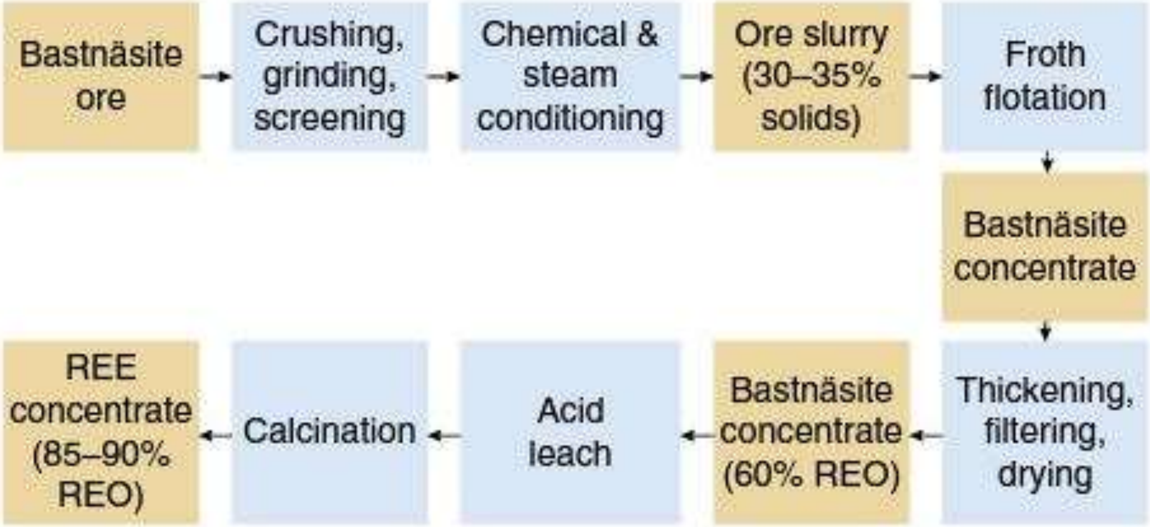
* i.e. low grade = large amount of rock

Bastnäsite beneficiation flow diagram



Generalised bastnäsite beneficiation flow diagram, based upon the former Mountain Pass operation.

REE extraction from bastnäsite



Bastnäsite ore → Crushing, grinding, screening → Chemical & steam conditioning → Ore slurry (30–35% solids) → Froth flotation → Bastnäsite concentrate → Thickening, filtering, drying → Bastnäsite concentrate (60% REO) → Acid leach → Calcination → REE concentrate (85–90% REO)

Figure 13.7 Schematic summary of the beneficiation of bastnäsite ores.

REE extraction from bastnäsite

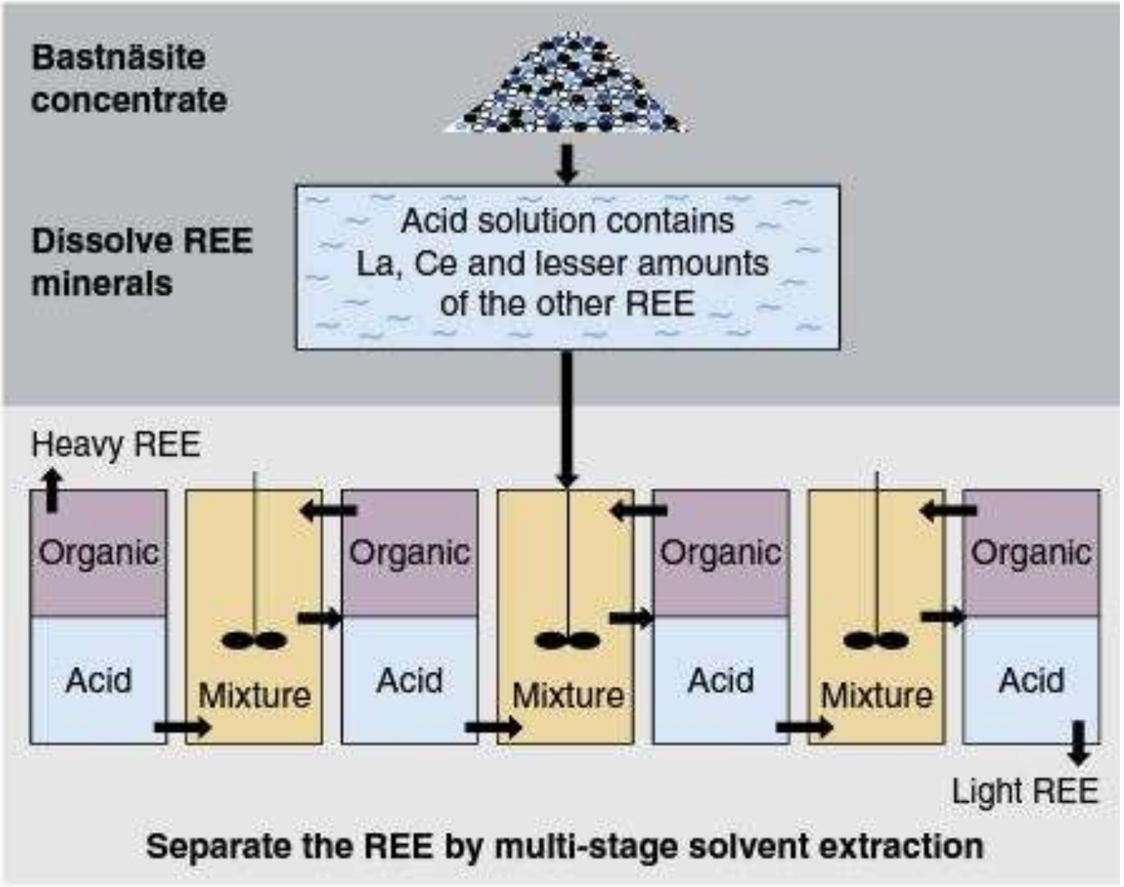
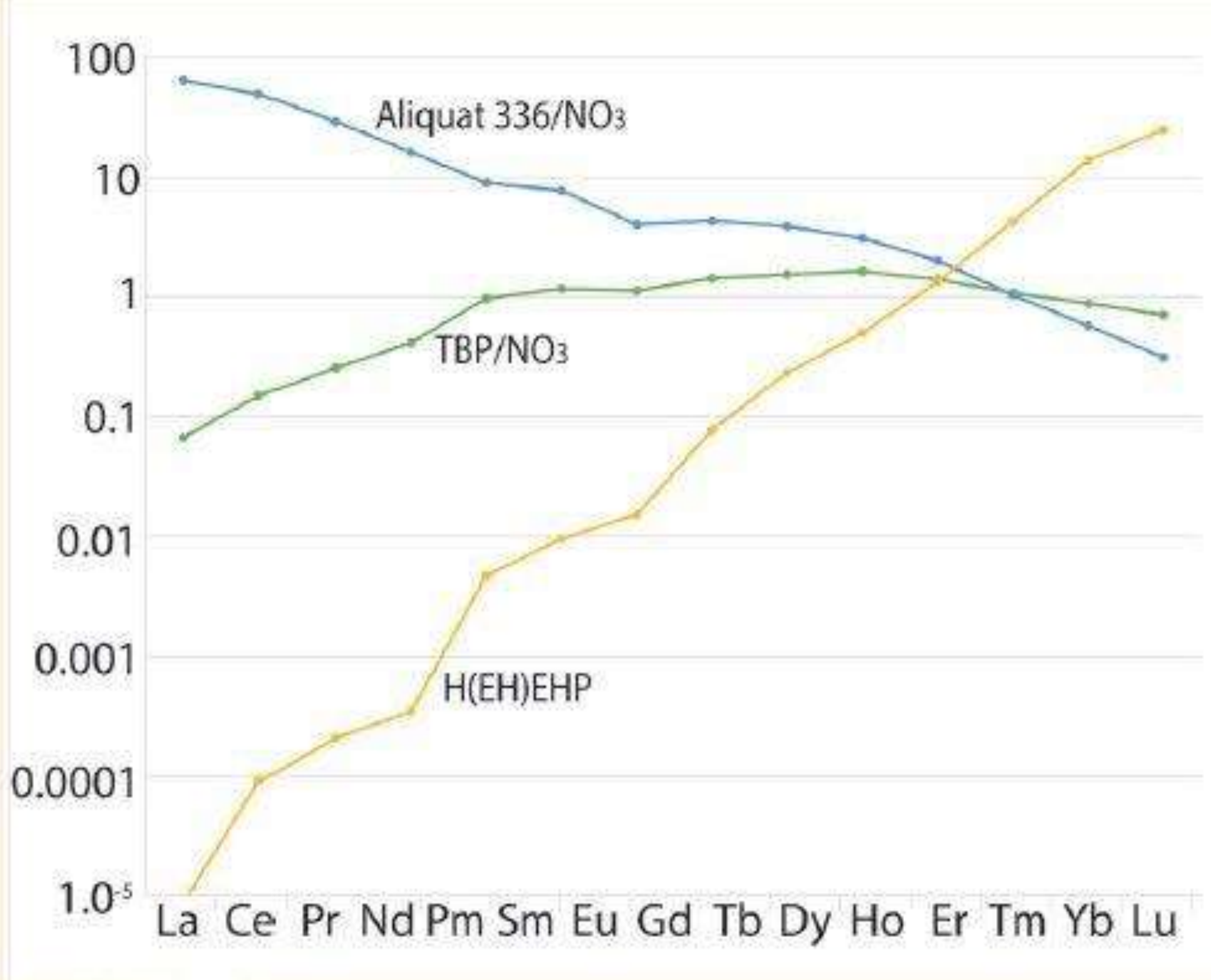


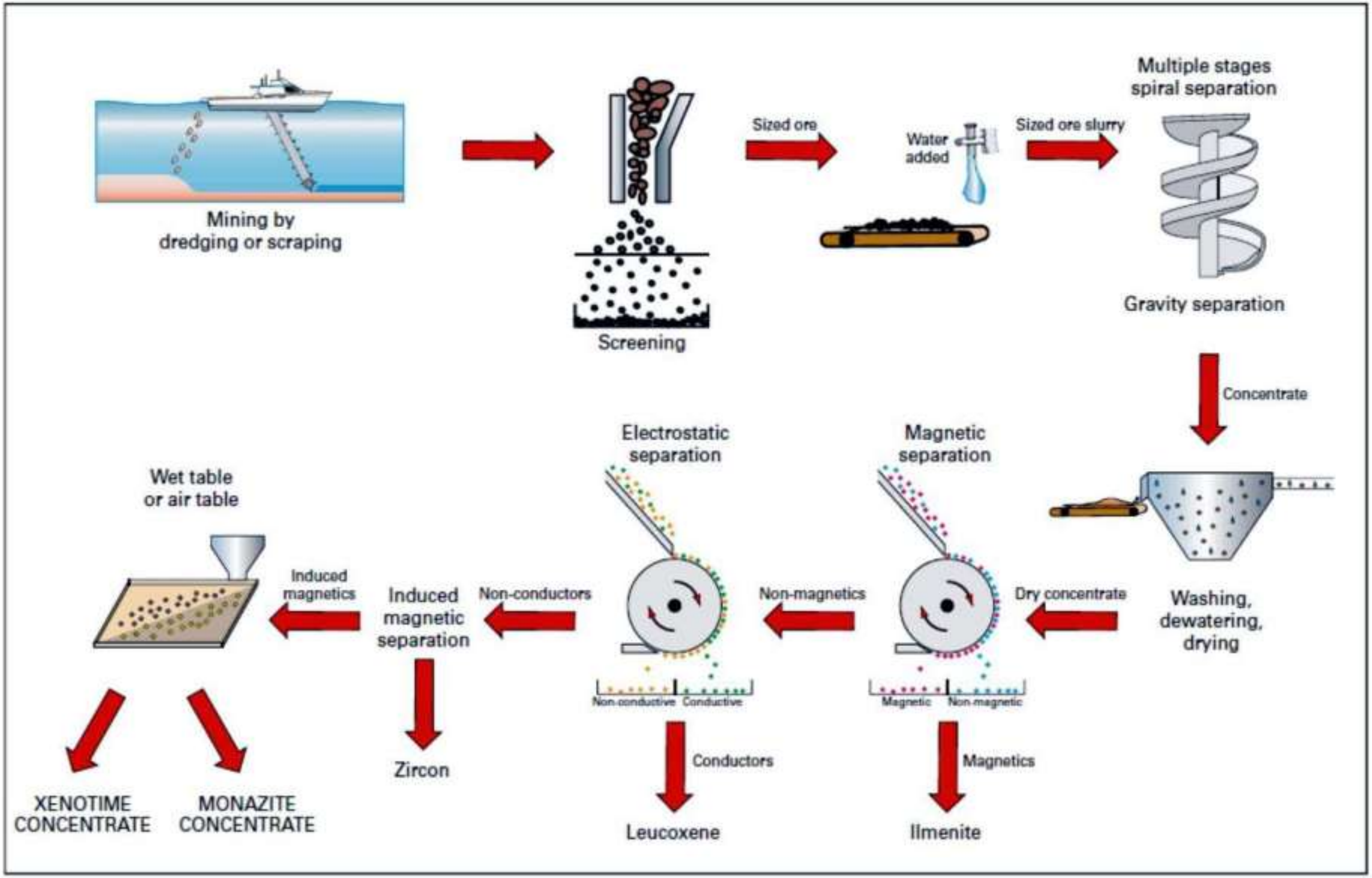
Figure 13.9 Schematic flowsheet for the extraction of rare earths from bastnäsite at Mountain Pass. (After Molycorp Inc., 2011b.)

REE extractants



Relative partition coefficients (*P*) of REE^{3+}, i.e. [$P(REE^{3+})$] for the three extractants: (1) 2-Ethylhexyl phosphonic acid, mono-2-ethylhexyl ester (H(EH)EHP). (2) Tributyl phosphate in a nitrate medium (TBP/NO_3). (3) Aliquat 336 in a nitrate medium (Aliquat^{336}/NO_3). The scale is normalized to a partition of one for Y. The larger the difference of $P(REE^{3+})$ between two adjacent REEs, the more selective the extractant. MODIFIED FROM LUCAS ET AL. (2015).

Monazite and xenotime extraction from placer deposits



Generalised flow diagram for extraction of monazite and xenotime from placer deposits.

Monazite and xenotime extraction from placer deposits

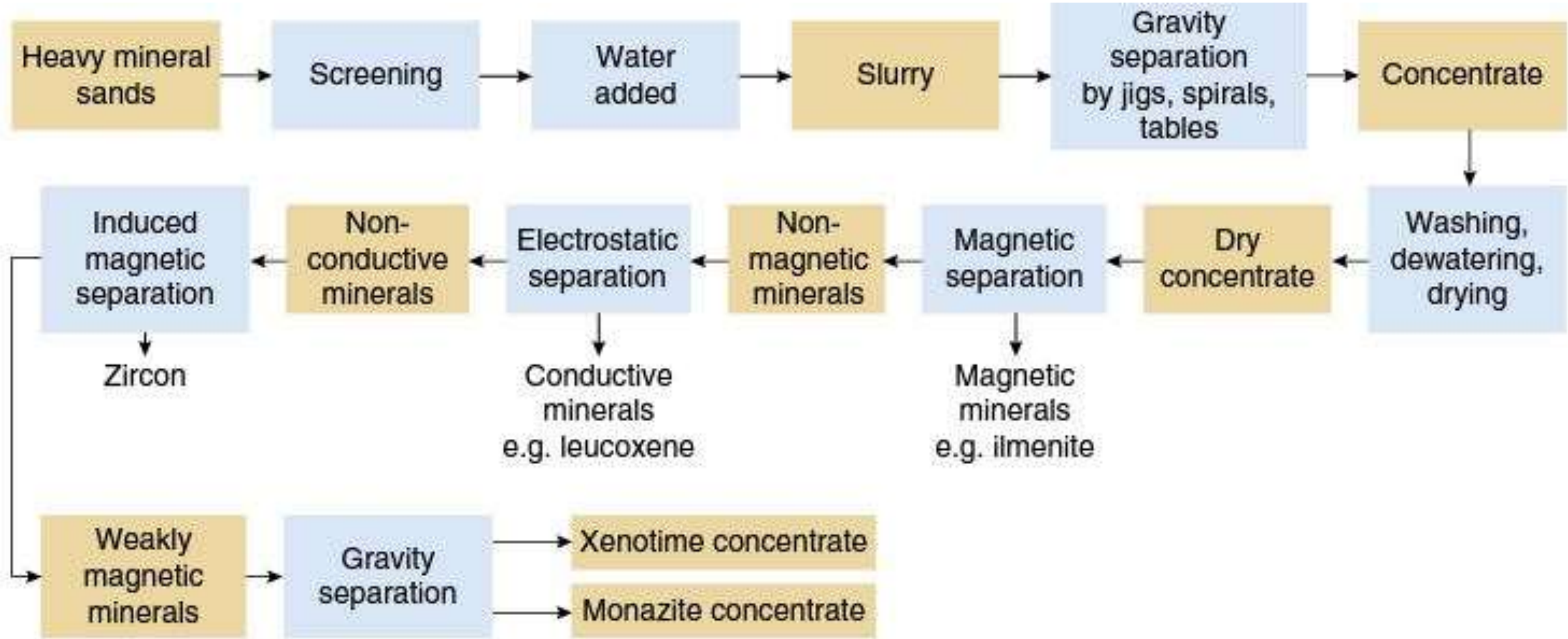
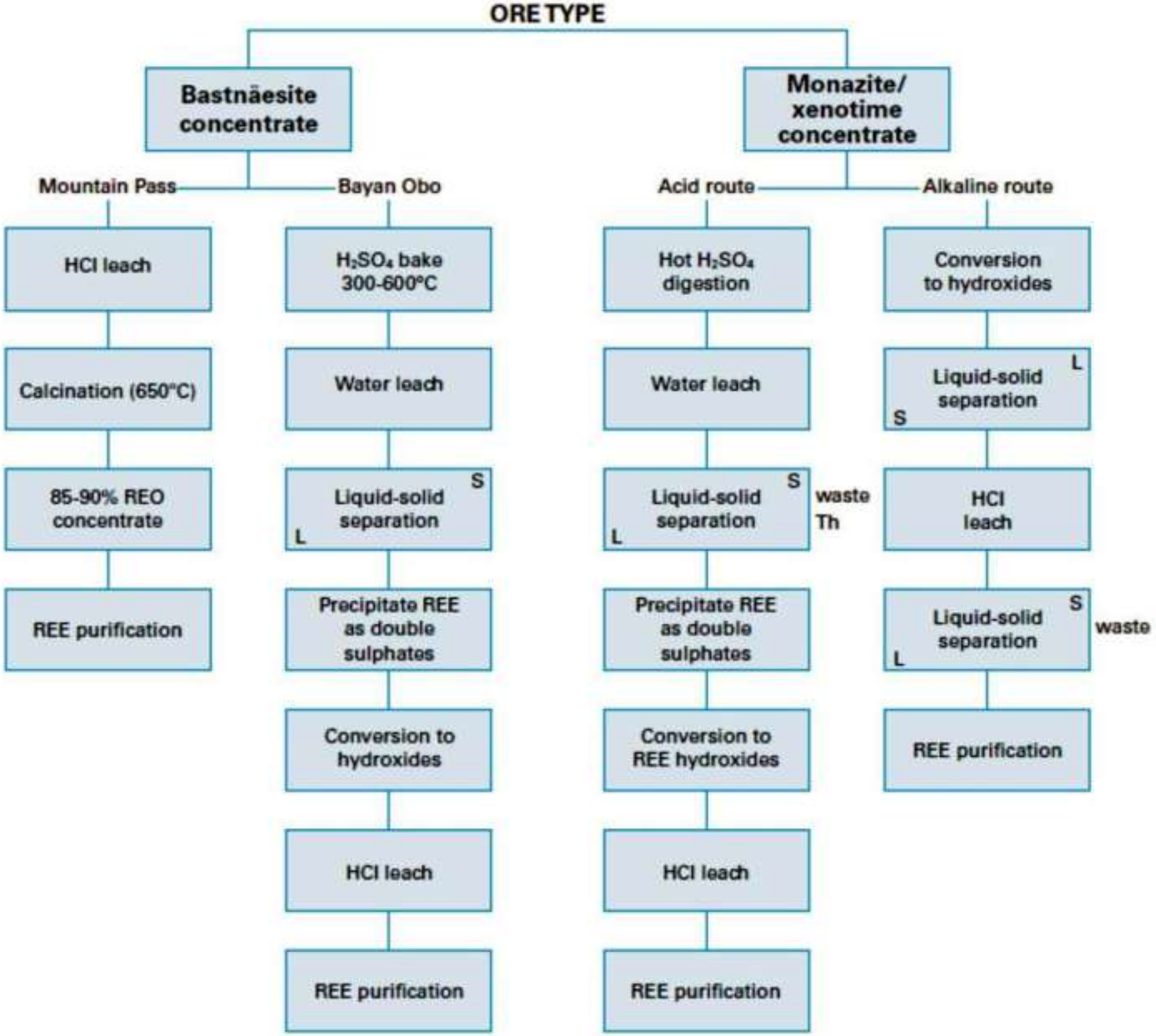
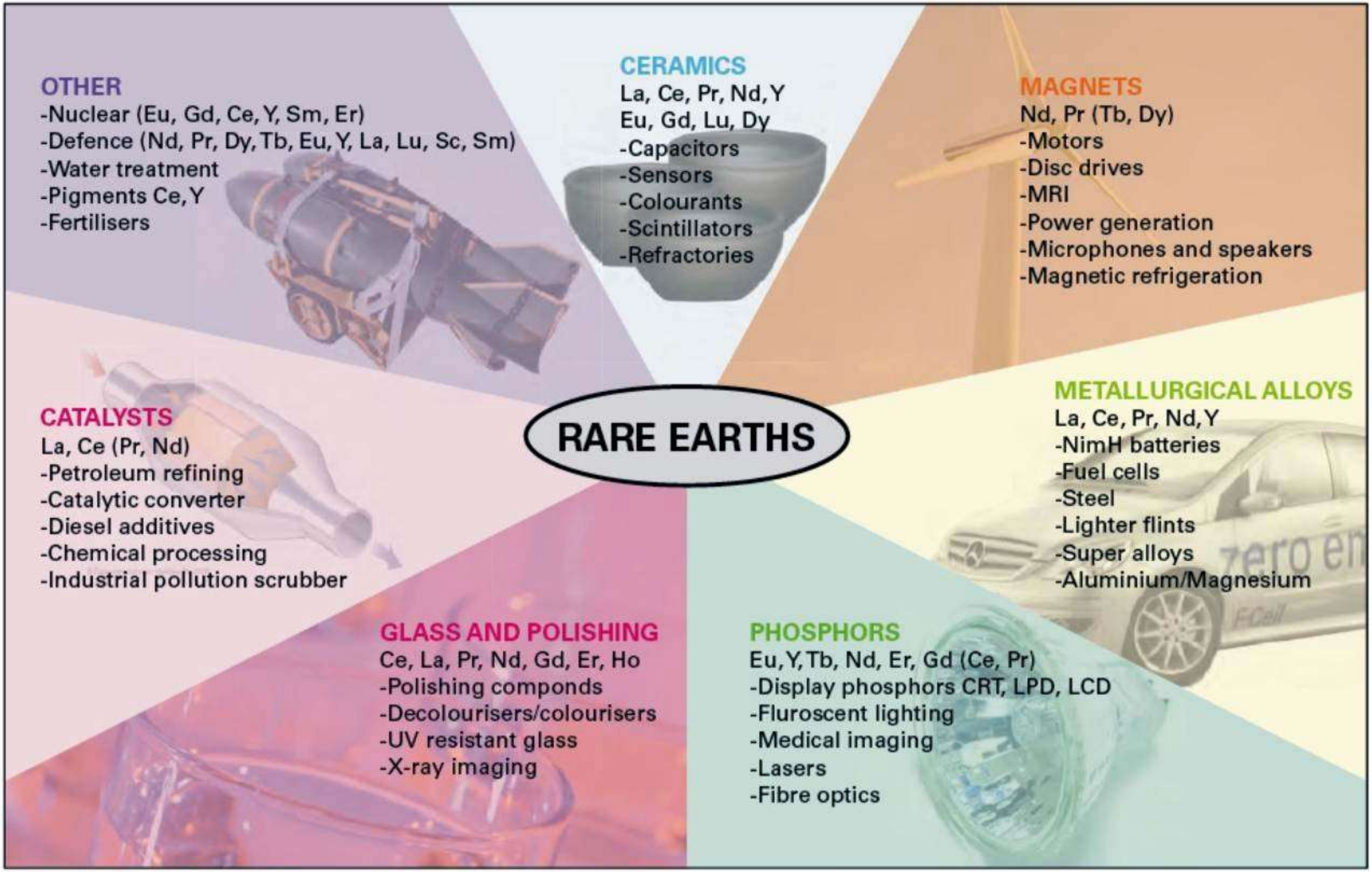


Figure 13.8 Schematic summary for the extraction of monazite and xenotime from heavy mineral sands.



Examples of processing routes for the separation of individual REE from the major REE-bearing minerals. H_2SO_4, sulphuric acid; HCl, hydrochloric acid (adapted from Chegwidden and Kingsnorth, 2002).



RARE EARTHS

CERAMICS
La, Ce, Pr, Nd, Y
Eu, Gd, Lu, Dy
- Capacitors
- Sensors
- Colourants
- Scintillators
- Refractories

MAGNETS
Nd, Pr (Tb, Dy)
- Motors
- Disc drives
- MRI
- Power generation
- Microphones and speakers
- Magnetic refrigeration

METALLURGICAL ALLOYS
La, Ce, Pr, Nd, Y
- NimH batteries
- Fuel cells
- Steel
- Lighter flints
- Super alloys
- Aluminium/Magnesium

PHOSPHORS
Eu, Y, Tb, Nd, Er, Gd (Ce, Pr)
- Display phosphors CRT, LPD, LCD
- Fluroscent lighting
- Medical imaging
- Lasers
- Fibre optics

GLASS AND POLISHING
Ce, La, Pr, Nd, Gd, Er, Ho
- Polishing componds
- Decolourisers/colourisers
- UV resistant glass
- X-ray imaging

CATALYSTS
La, Ce (Pr, Nd)
- Petroleum refining
- Catalytic converter
- Diesel additives
- Chemical processing
- Industrial pollution scrubber

OTHER
- Nuclear (Eu, Gd, Ce, Y, Sm, Er)
- Defence (Nd, Pr, Dy, Tb, Eu, Y, La, Lu, Sc, Sm)
- Water treatment
- Pigments Ce, Y
- Fertilisers

REE – industrial uses

- catalysts
- metallurgy
- electrical industry, electronics and magnets,
- rechargeable batteries
- super-conductor industry
- phosphors and medical radiography
- glass and ceramic industries, abrasive
- chemical industry
- nuclear power generation
- magnetic refrigeration
- Solid oxide fuel cells (SOFC)
- wastewater treatment

REE – industrial uses

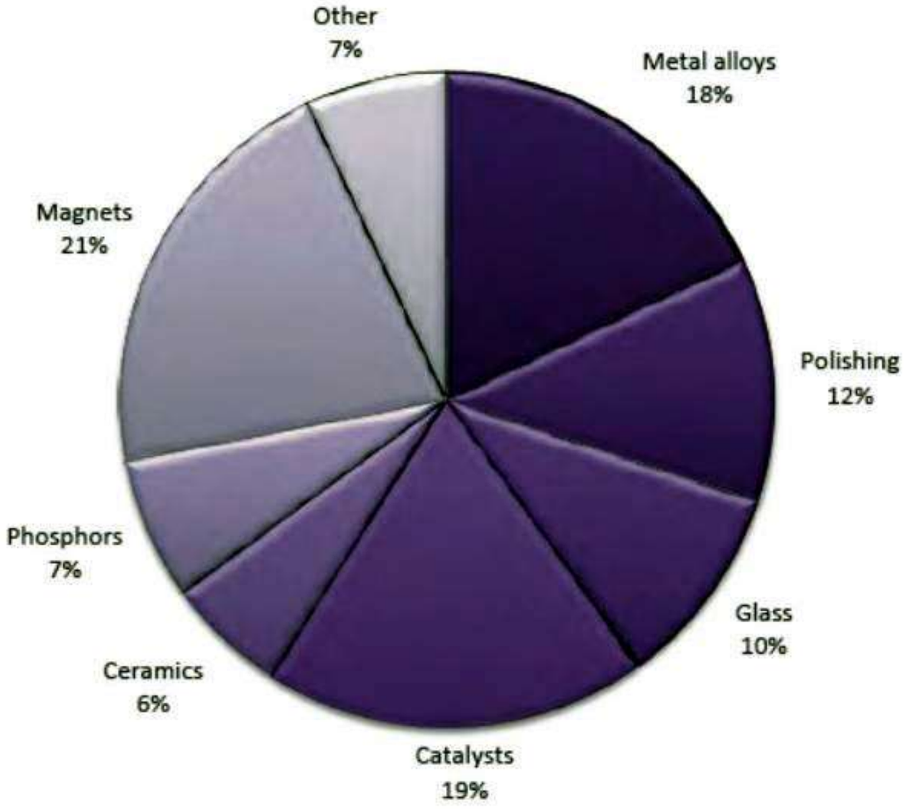


Figure REE consumption by volume (Kingsnorth, 2009).

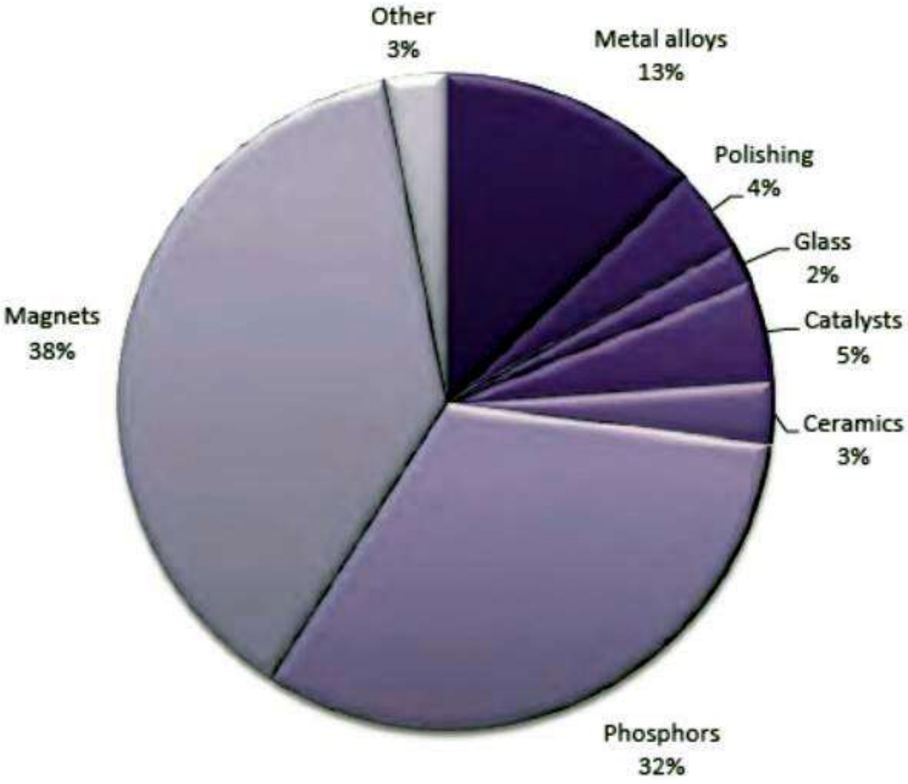


Figure REE consumption by value (Kingsnorth, 2009).

Rare Earth Elements in Consumer Goods

Television
Europium, Cerium

Computer
Cerium
Neodymium

Automobile
Lanthanum, Cerium, Yttrium, Dysprosium

Mobile Phone
Neodymium
Cerium

Aircraft
Lanthanum, Cerium, Yttrium, Dysprosium, Europium

Wind Turbines
Neodymium, Dysprosium

Solar Panels
Lanthanum

Welding Goggles
Neodymium

Fluorescent Lighting
Terbium

REE – industrial uses

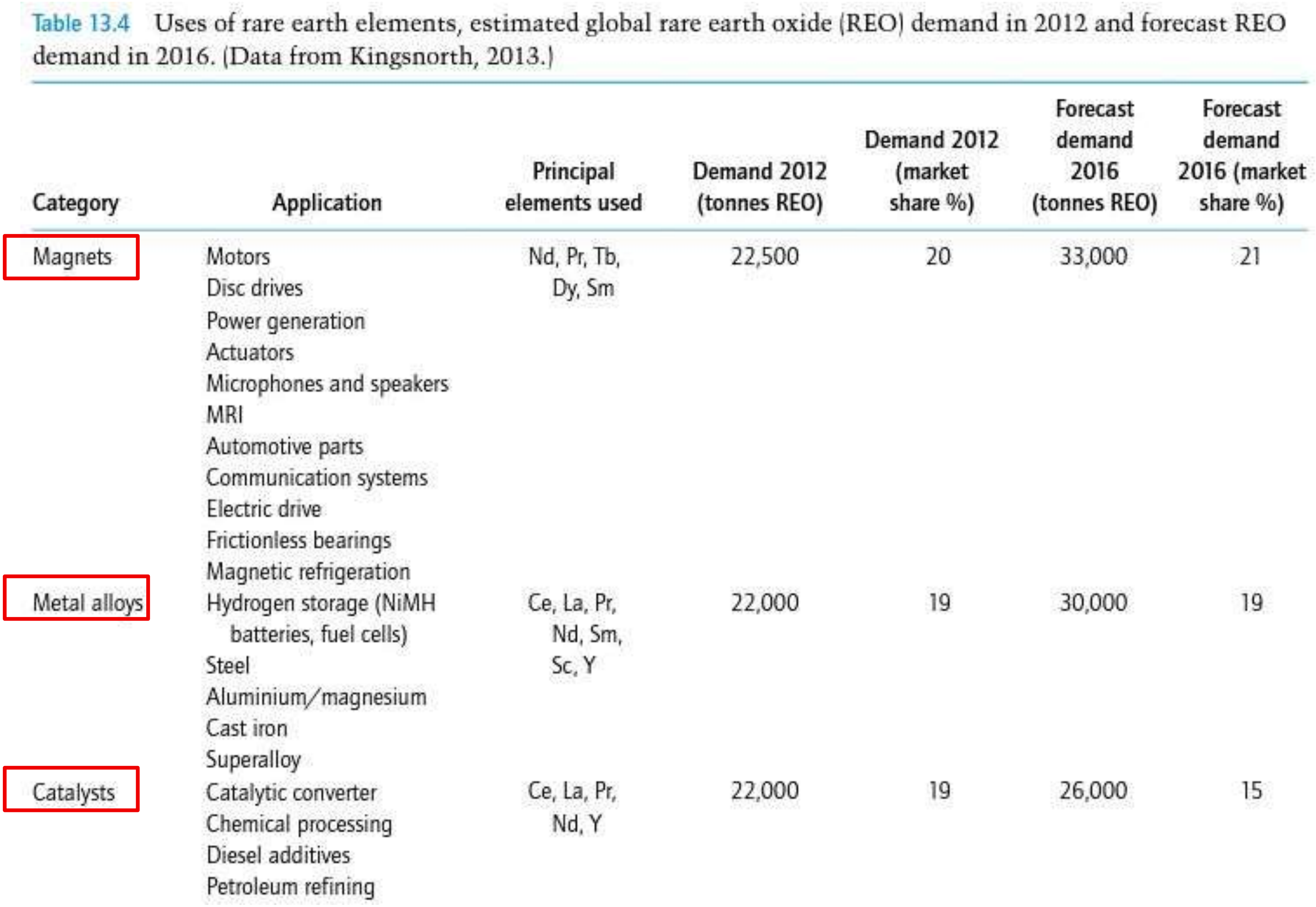


Table 13.4 Uses of rare earth elements, estimated global rare earth oxide (REO) demand in 2012 and forecast REO demand in 2016. (Data from Kingsnorth, 2013.)

Category	Application	Principal elements used	Demand 2012 (tonnes REO)	Demand 2012 (market share %)	Forecast demand 2016 (tonnes REO)	Forecast demand 2016 (market share %)
Magnets	Motors Disc drives Power generation Actuators Microphones and speakers MRI Automotive parts Communication systems Electric drive Frictionless bearings Magnetic refrigeration	Nd, Pr, Tb, Dy, Sm	22,500	20	33,000	21
Metal alloys	Hydrogen storage (NiMH batteries, fuel cells) Steel Aluminium/magnesium Cast iron Superalloy	Ce, La, Pr, Nd, Sm, Sc, Y	22,000	19	30,000	19
Catalysts	Catalytic converter Chemical processing Diesel additives Petroleum refining	Ce, La, Pr, Nd, Y	22,000	19	26,000	15

REE – industrial uses

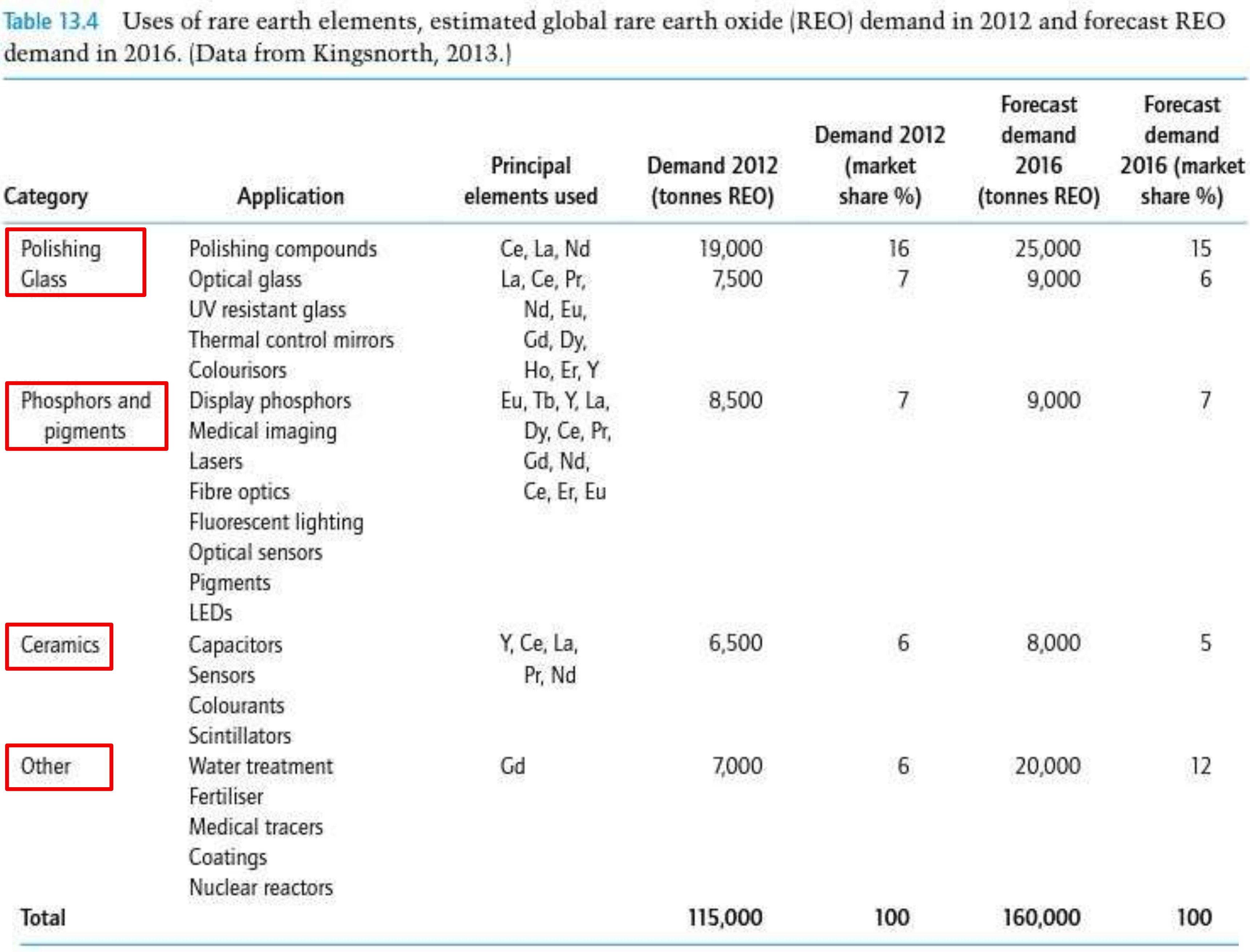


Table 13.4 Uses of rare earth elements, estimated global rare earth oxide (REO) demand in 2012 and forecast REO demand in 2016. (Data from Kingsnorth, 2013.)

Category	Application	Principal elements used	Demand 2012 (tonnes REO)	Demand 2012 (market share %)	Forecast demand 2016 (tonnes REO)	Forecast demand 2016 (market share %)
Polishing	Polishing compounds	Ce, La, Nd	19,000	16	25,000	15
Glass	Optical glass UV resistant glass Thermal control mirrors Colourisors	La, Ce, Pr, Nd, Eu, Gd, Dy, Ho, Er, Y	7,500	7	9,000	6
Phosphors and pigments	Display phosphors Medical imaging Lasers Fibre optics Fluorescent lighting Optical sensors Pigments LEDs	Eu, Tb, Y, La, Dy, Ce, Pr, Gd, Nd, Ce, Er, Eu	8,500	7	9,000	7
Ceramics	Capacitors Sensors Colourants Scintillators	Y, Ce, La, Pr, Nd	6,500	6	8,000	5
Other	Water treatment Fertiliser Medical tracers Coatings Nuclear reactors	Gd	7,000	6	20,000	12
Total			**115,000**	**100**	**160,000**	**100**

REE applications in the automotive industry

Rare Earth Elements in the Toyota Prius

Toyota Prius

LCD Screen
- Europium
- Yttrium
- Cerium

Glass and Mirrors Polishing Powder
- Cerium

UV Cut Glass
- Cerium

Diesel Fuel Additive
- Cerium
- Lanthanum

Component Sensors
- Yttrium

Hybrid NiMH Battery
- Lanthanum
- Cerium

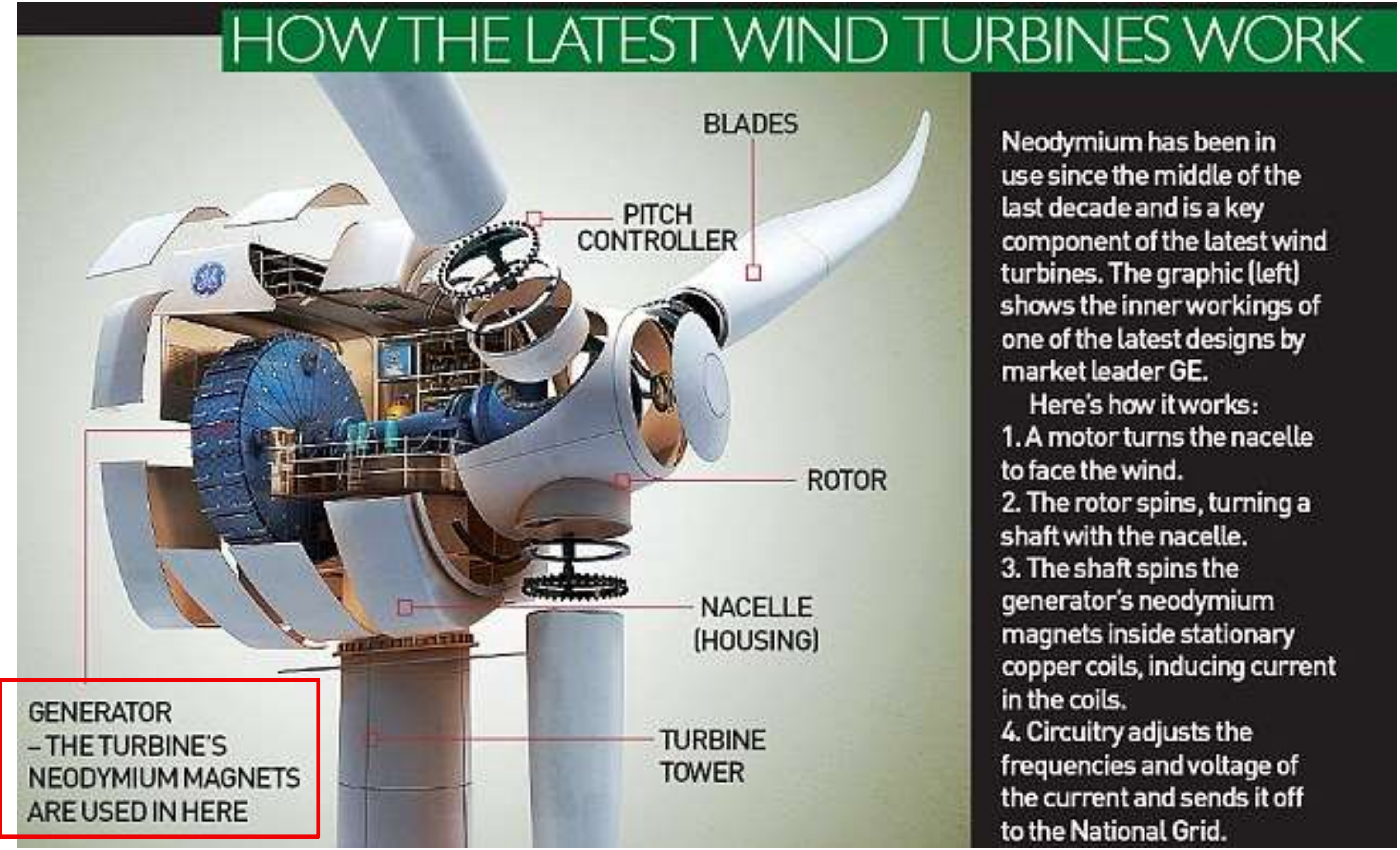
Hybrid Electric Motor/Generator
- Neodymium
- Praseodymium
- Dysprosium
- Terbium

Catalytic Converter
- Cerium
- Lanthanum

Headlight Glass
- Neodymium

25+ Electric Motors
- Neodymium magnets

REE applications in wind turbines



HOW THE LATEST WIND TURBINES WORK

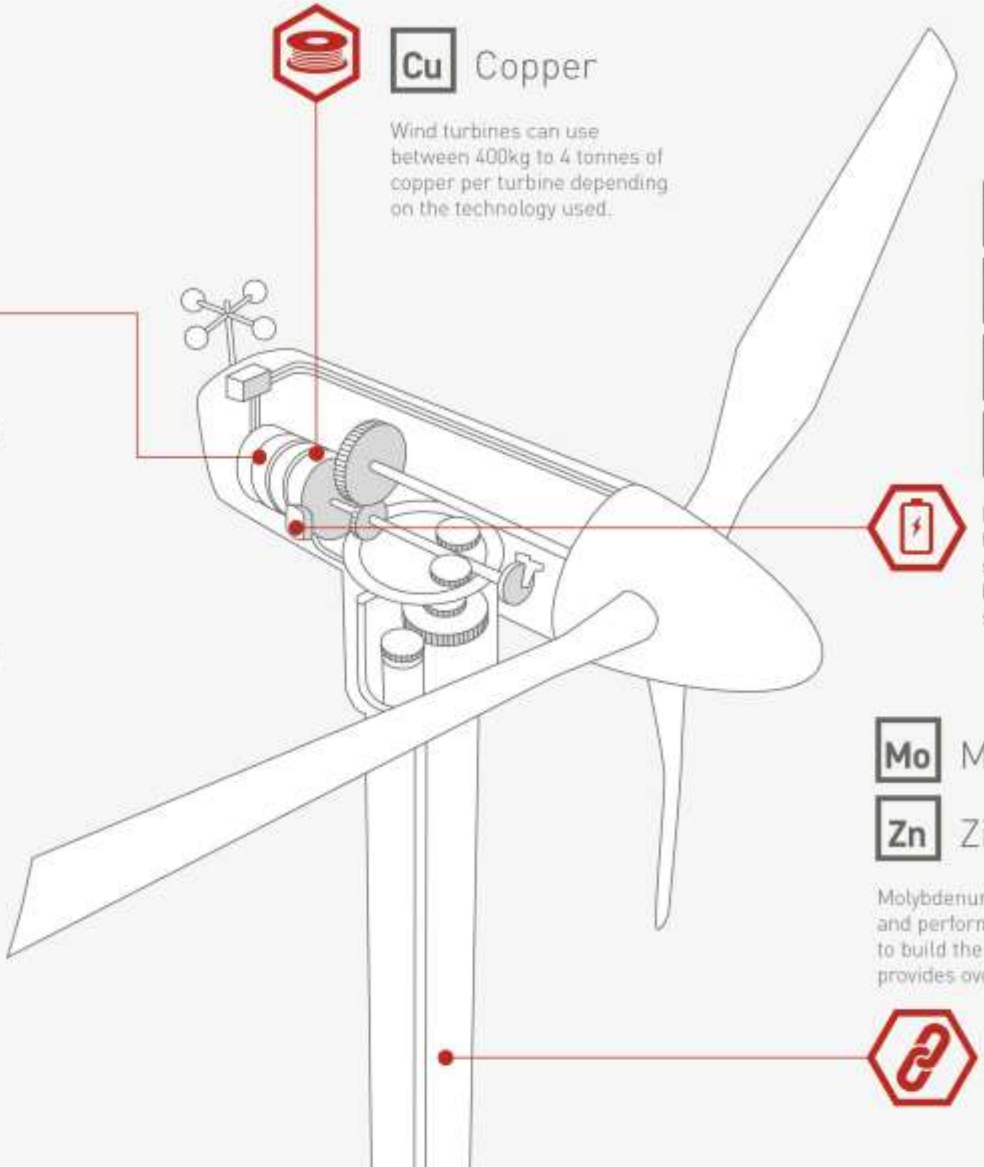
Neodymium has been in use since the middle of the last decade and is a key component of the latest wind turbines. The graphic (left) shows the inner workings of one of the latest designs by market leader GE.

Here's how it works:

1. A motor turns the nacelle to face the wind.
2. The rotor spins, turning a shaft with the nacelle.
3. The shaft spins the generator's neodymium magnets inside stationary copper coils, inducing current in the coils.
4. Circuitry adjusts the frequencies and voltage of the current and sends it off to the National Grid.

PROVIDING EFFICIENT, LOW CARBON ENERGY

ICMM
International Council
on Mining & Metals



Cu Copper

Wind turbines can use between 400kg to 4 tonnes of copper per turbine depending on the technology used.

Nd Neodymium
Fe Iron
B Boron
Dy Dysprosium

Neodymium, iron, boron and dysprosium are used in the permanent magnet generators that many wind turbines now employ.

Pb Lead
Li Lithium
Ni Nickel
Na Sodium

Battery energy storage supports the integration of renewables and stabilization of the electricity grid, based on lead, lithium, nickel or sodium technologies.

Mo Molybdenum
Zn Zinc

Molybdenum and zinc enhance the longevity and performance of the high-tech steel used to build the tower. Thermally-sprayed zinc provides over 20 years of corrosion protection.

Properties of Nd-Fe-B magnets

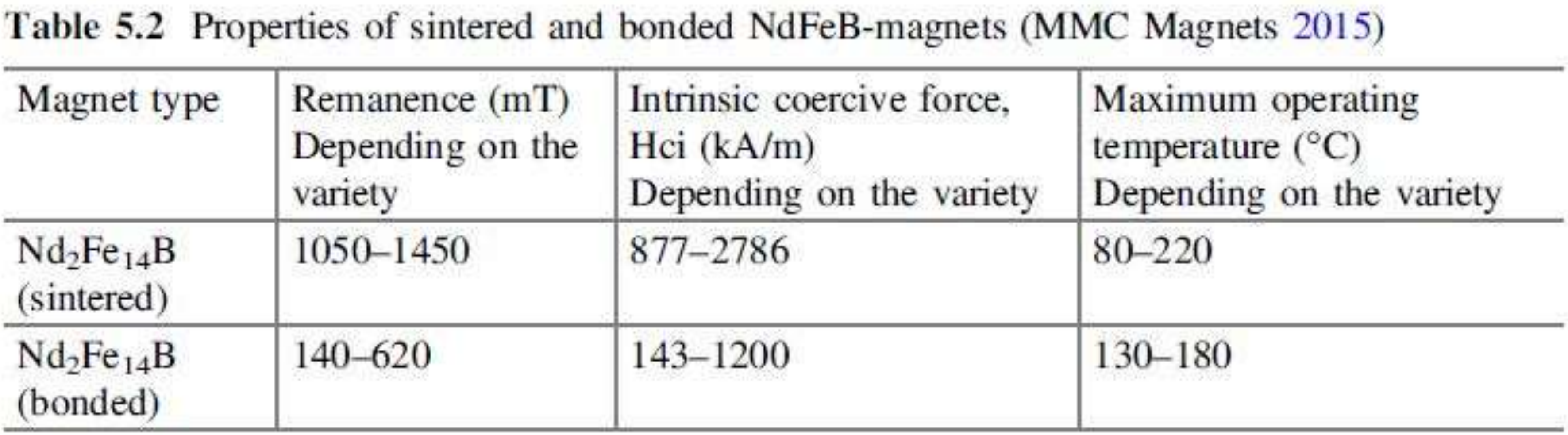


Table 5.2 Properties of sintered and bonded NdFeB-magnets (MMC Magnets 2015)

Magnet type	Remanence (mT) Depending on the variety	Intrinsic coercive force, Hci (kA/m) Depending on the variety	Maximum operating temperature (°C) Depending on the variety
$Nd_2Fe_{14}B$ (sintered)	1050–1450	877–2786	80–220
$Nd_2Fe_{14}B$ (bonded)	140–620	143–1200	130–180

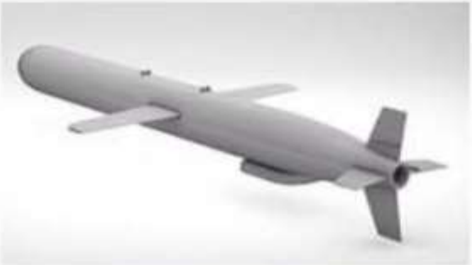
Rare Earth Elements in the Military

Predator Drone

Neodymium, Samarium
Electric Motors and Guidance

Smart Bomb

Neodymium, Samarium
Electric Motors and Guidance



Tomahawk Cruise Missile

Neodymium, Samarium
Electric Motors and Guidance

Night Vision Goggles

Terbium, Erbium, Gadolinium
Optical Lenses

F-22 Fighter Jet

Europium, Yttrium Terbium, Erbium
Optical Systems, Visuals and Fiber Optics

Bullet Proof Vest

Yttrium
Hardened Ceramics

Bradley Tank

Yttrium
Hardened Ceramics

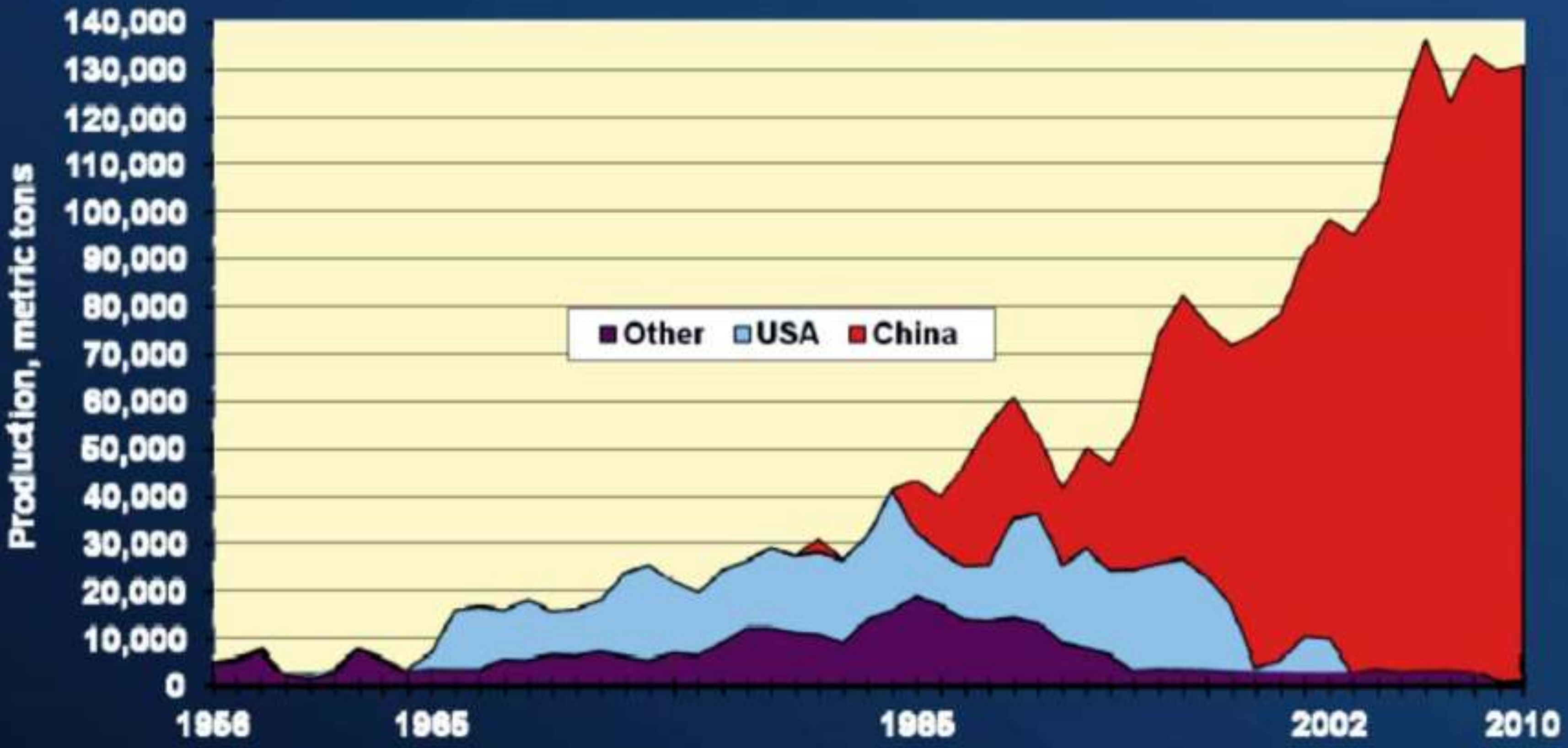
Radar Detection

Europium, Lutetium
Signal Amplification

Nuclear Submarine

Europium, Lutetium
Sonar Detection

REO Production Trends – 1956 to 2010



Monazite-placer era | Mountain Pass era | Chinese era ⟶ ?

Sources: USGS Fact Sheet 087-02 updated with recent USGS Minerals Yearbook data

USGS

Production of REO between 1992-2010

Chinese and world production of REO between 1992–2010 (World Minerals Statistics Database, BGS).

REE – imports and exports

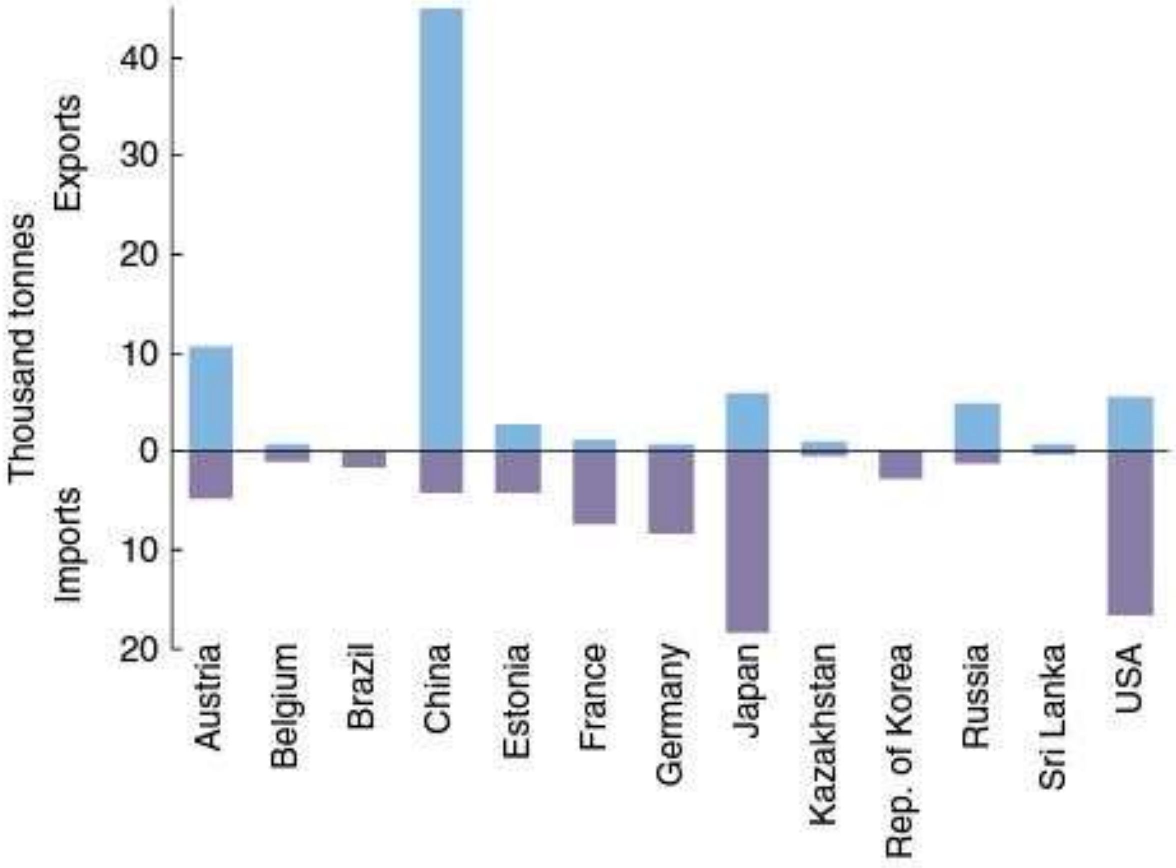


Figure 13.11 Imports and exports of rare earth metals and compounds, 2009. (Data from British Geological Survey World Mineral Statistics Database and UN Comtrade, 2013.)

REE production and estimated reserves

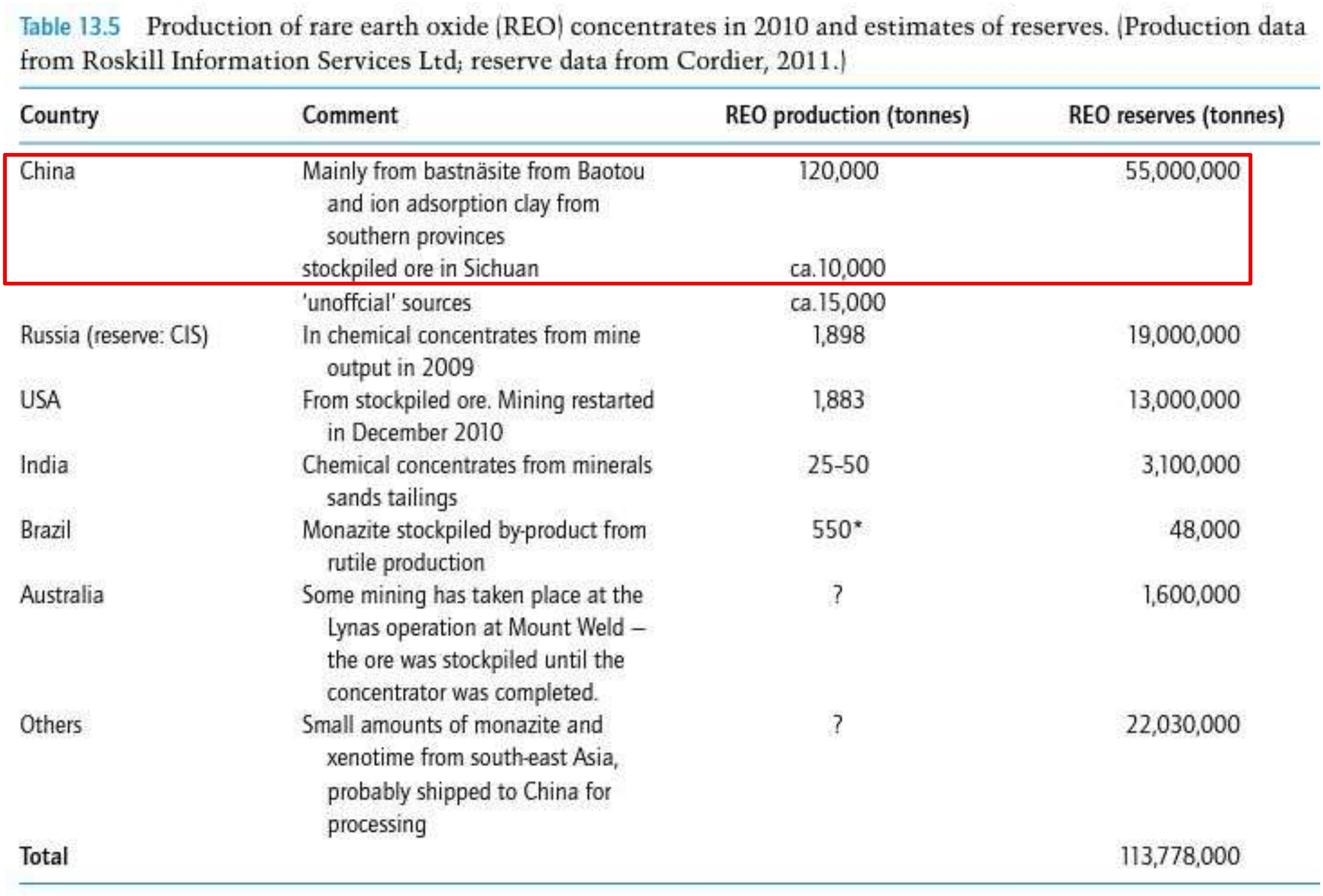
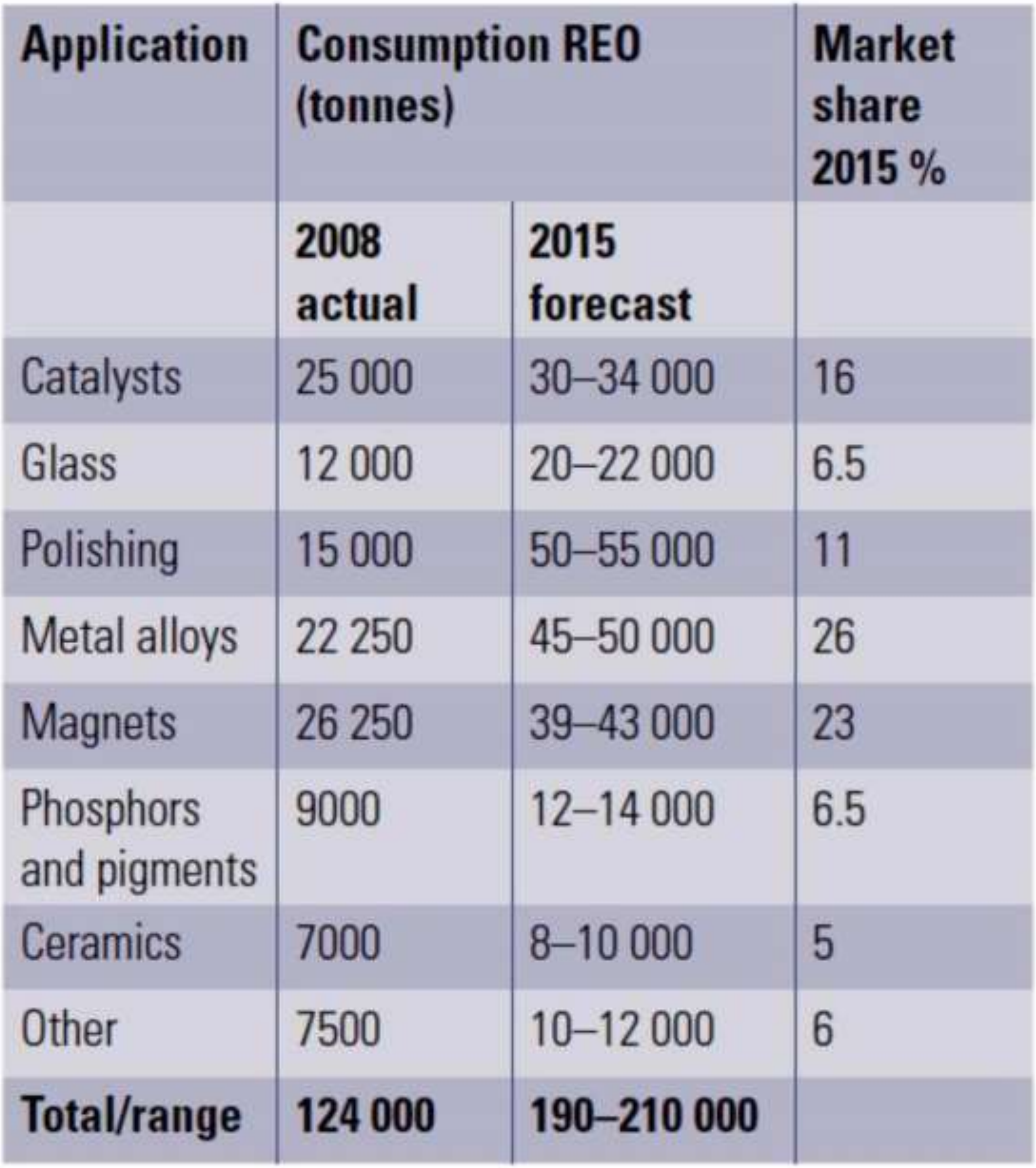


Table 13.5 Production of rare earth oxide (REO) concentrates in 2010 and estimates of reserves. (Production data from Roskill Information Services Ltd; reserve data from Cordier, 2011.)

Country	Comment	REO production (tonnes)	REO reserves (tonnes)
China	Mainly from bastnäsite from Baotou and ion adsorption clay from southern provinces	120,000	55,000,000
	stockpiled ore in Sichuan	ca.10,000	
	'unoffcial' sources	ca.15,000	
Russia (reserve: CIS)	In chemical concentrates from mine output in 2009	1,898	19,000,000
USA	From stockpiled ore. Mining restarted in December 2010	1,883	13,000,000
India	Chemical concentrates from minerals sands tailings	25-50	3,100,000
Brazil	Monazite stockpiled by-product from rutile production	550*	48,000
Australia	Some mining has taken place at the Lynas operation at Mount Weld – the ore was stockpiled until the concentrator was completed.	?	1,600,000
Others	Small amounts of monazite and xenotime from south-east Asia, probably shipped to China for processing	?	22,030,000
Total			113,778,000

REO application and consumption



Application	Consumption REO (tonnes)		Market share 2015 %
	2008 actual	**2015 forecast**	
Catalysts	25 000	30–34 000	16
Glass	12 000	20–22 000	6.5
Polishing	15 000	50–55 000	11
Metal alloys	22 250	45–50 000	26
Magnets	26 250	39–43 000	23
Phosphors and pigments	9000	12–14 000	6.5
Ceramics	7000	8–10 000	5
Other	7500	10–12 000	6
Total/range	**124 000**	**190–210 000**	

Global demand for REE in 2008 and 2015 (Kingsnorth, 2010).

REE - prices

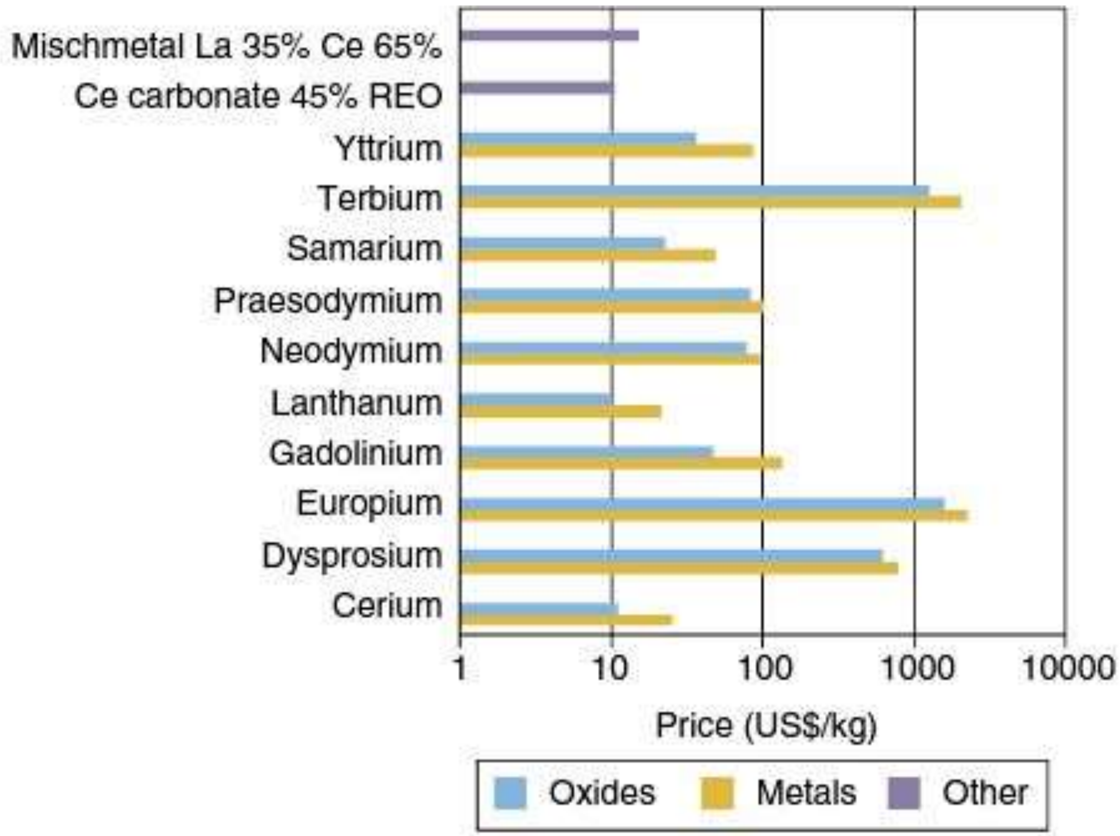
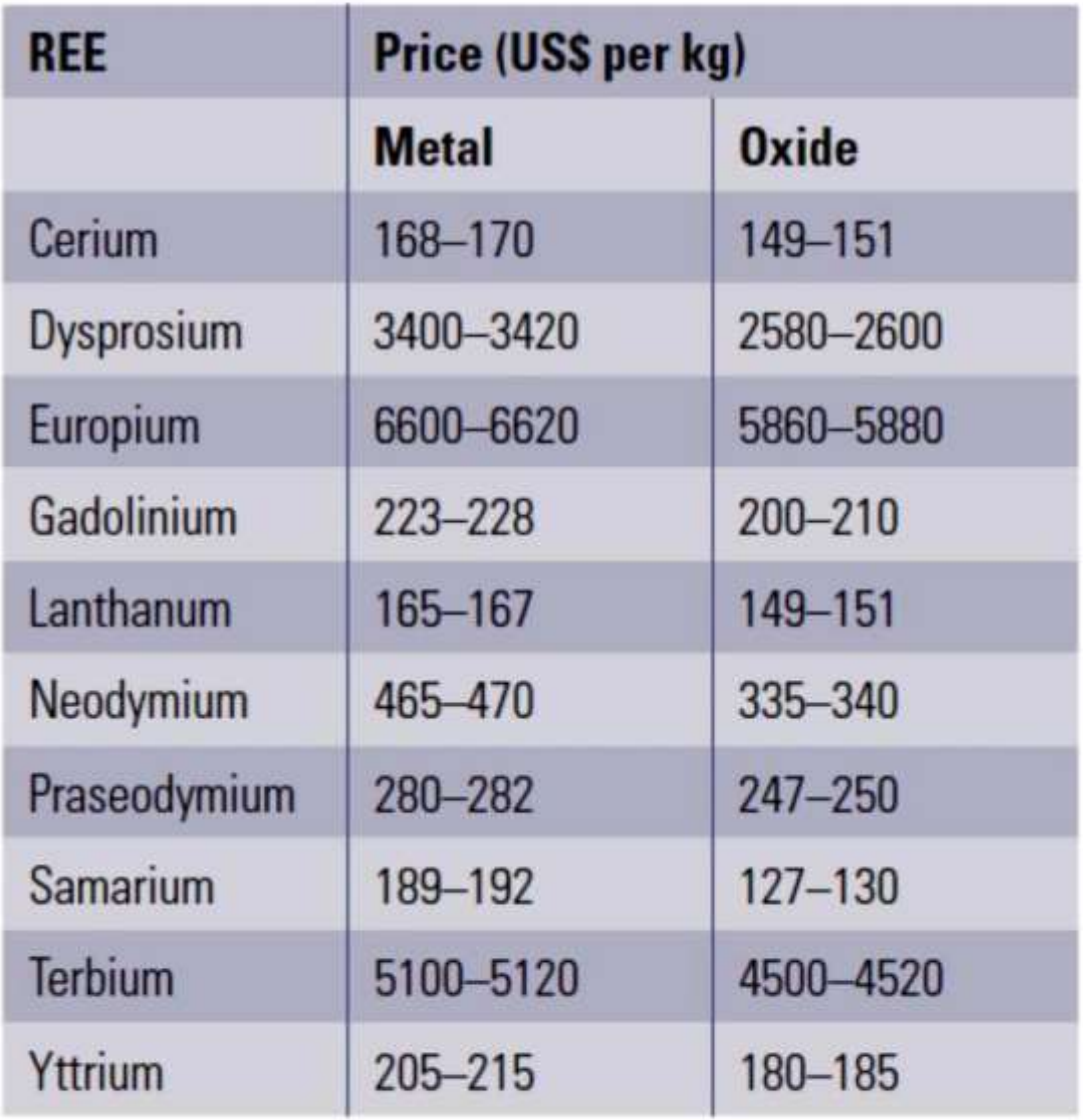


Figure 13.12 Prices of rare earth metals, oxides, mischmetal and mixed light REE carbonate in January 2013. Prices are FOB China, 99% metal min., except Y 99.9% min.; oxide: FOB China, 99% min., except Eu 99.9%, Y, 99.999%. (Data from Metal Pages, www.metal-pages.com.)

REO and metal prices (2011)



REE	Price (US$ per kg)	
	Metal	**Oxide**
Cerium	168–170	149–151
Dysprosium	3400–3420	2580–2600
Europium	6600–6620	5860–5880
Gadolinium	223–228	200–210
Lanthanum	165–167	149–151
Neodymium	465–470	335–340
Praseodymium	280–282	247–250
Samarium	189–192	127–130
Terbium	5100–5120	4500–4520
Yttrium	205–215	180–185

REO and metal prices on August 16th 2011. Prices shown are for a minimum 99% purity and are quoted in US$ per kilogram on an FOB China basis (Metal-pages, 2011).

LREE average prices

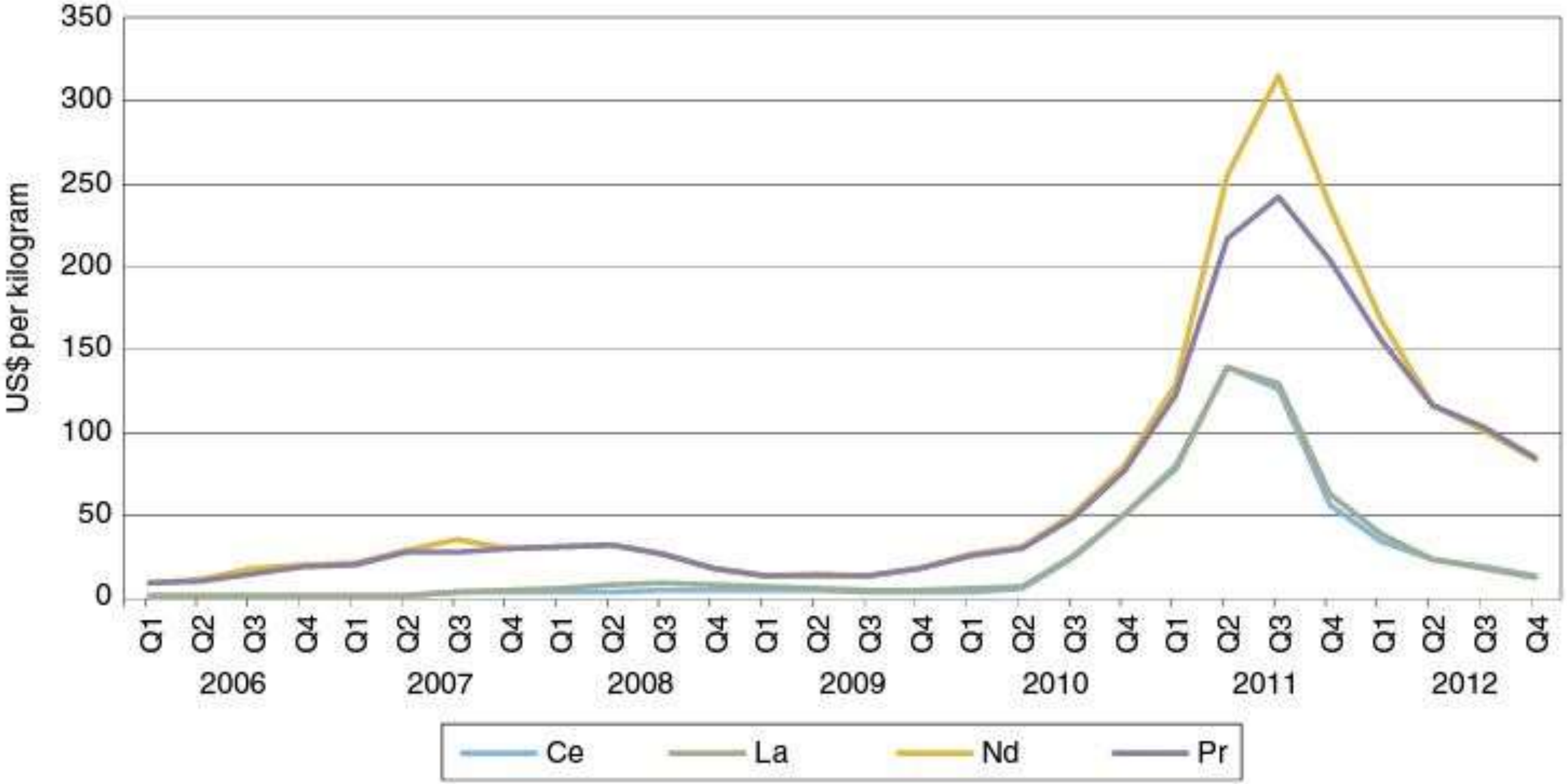


Figure 13.13 Quarterly average prices for selected LREE. Prices are for oxide FOB China 99% min. (Data from Metal Pages, www.metal-pages.com). Ce, cerium; La, lanthanum; Nd, neodymium; Pr, praseodymium.

HREE average prices

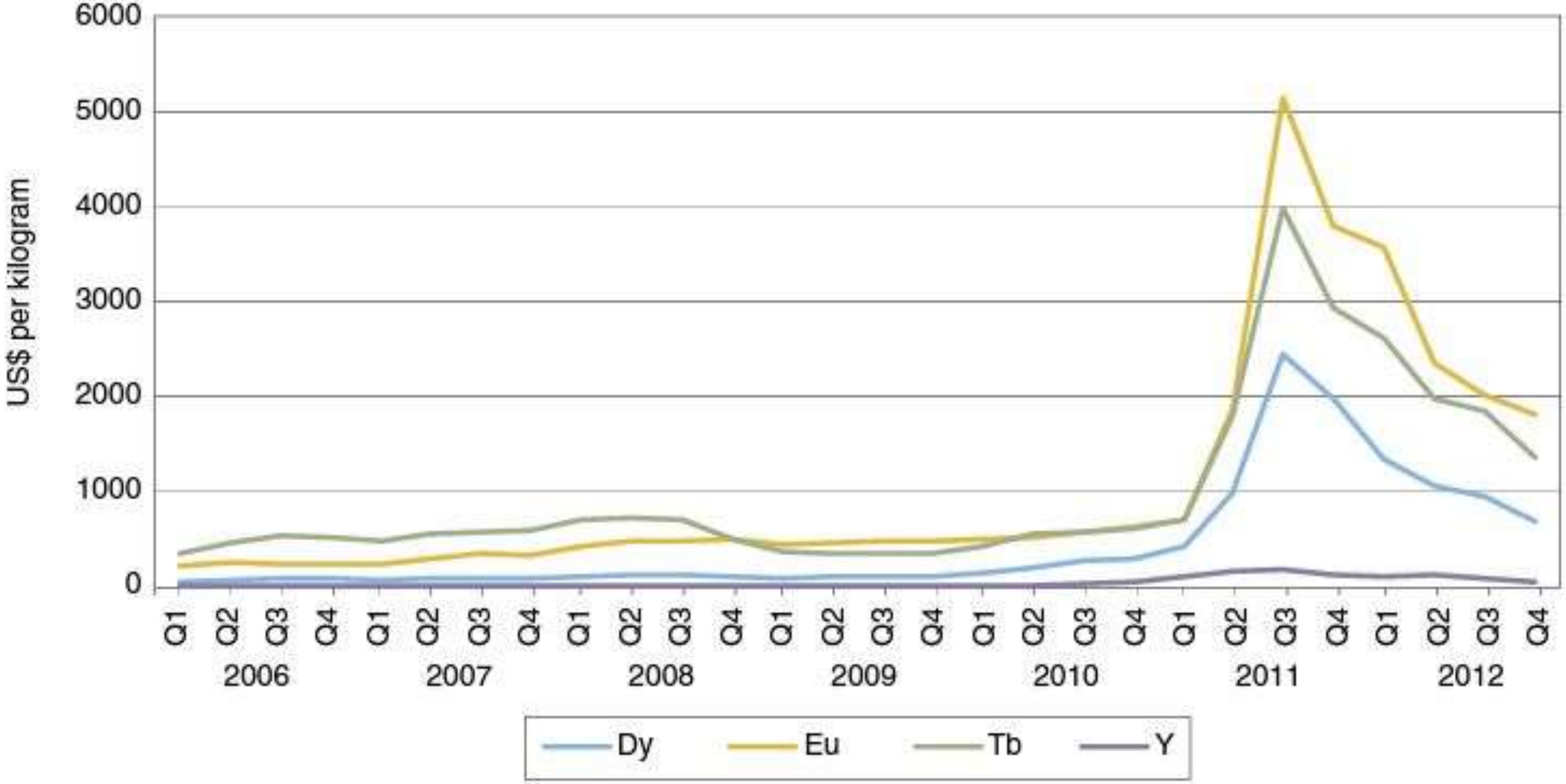


Figure 13.14 Quarterly average prices for selected HREE and Y. Prices are for oxide FOB China 99% min. for Dy and Tb, 99.9% min. for Eu, and 99.999% min. for Y. (Data from Metal Pages, www.metal-pages.com). Dy, dysprosium; Eu, europium; Tb, terbium; Y, yttrium.

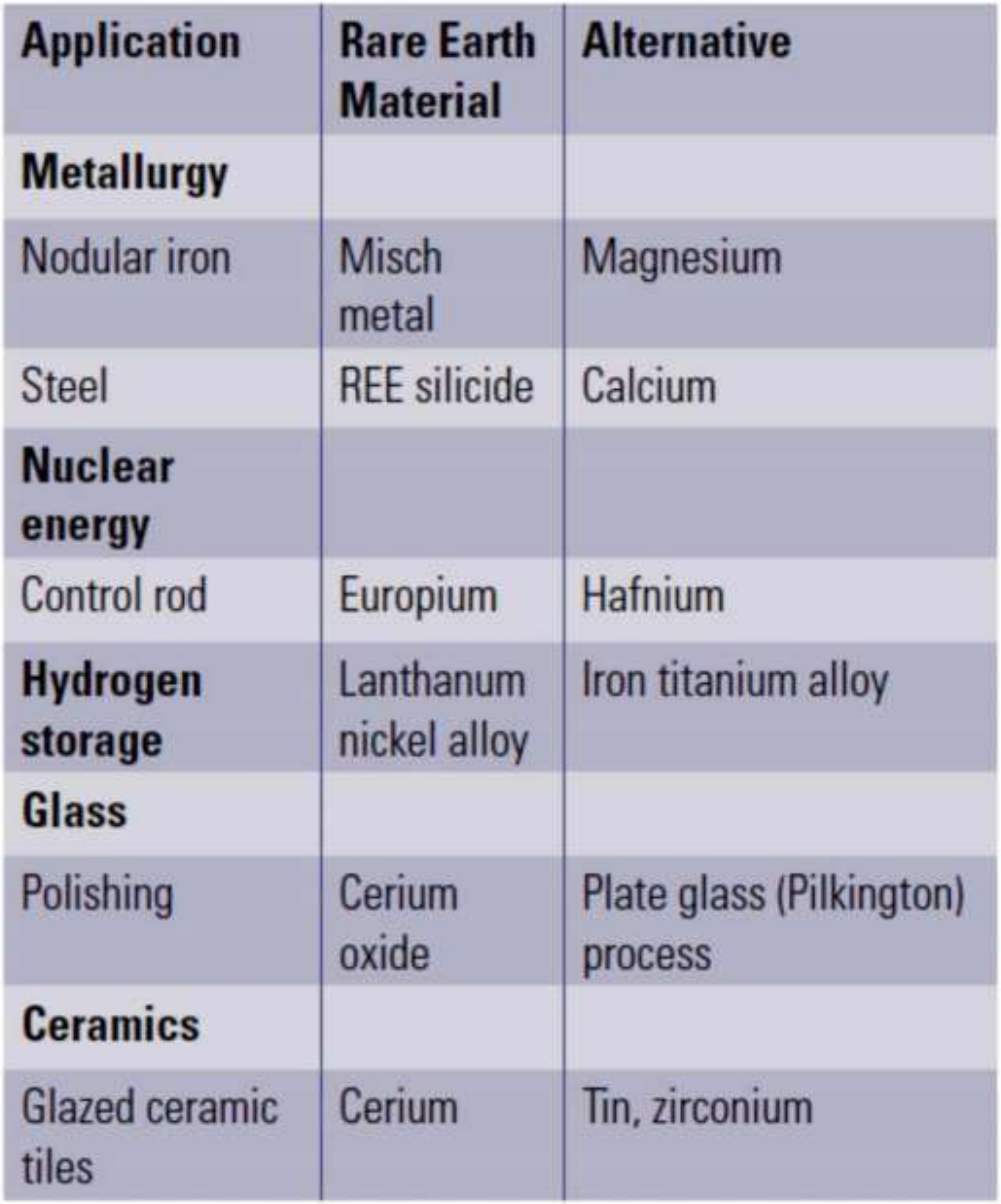
RECYCLING OF REE CONTAINING MATERIALS

The **recovery of REE** is today generally **complex and costly** in terms of **energy**:

- **different industrial applications**;
- **different duration** of an artifact (e.g. hard drives, electric/hybrid vehicle);
- the need for **complex separation-removal**.

The development of **recycling technologies** of REE containing waste will make this road more and more important, with less environmental problems (e.g. radioactivity, lower energy consumption).

Alternatives to REE



Application	Rare Earth Material	Alternative
Metallurgy		
Nodular iron	Misch metal	Magnesium
Steel	REE silicide	Calcium
Nuclear energy		
Control rod	Europium	Hafnium
Hydrogen storage	Lanthanum nickel alloy	Iron titanium alloy
Glass		
Polishing	Cerium oxide	Plate glass (Pilkington) process
Ceramics		
Glazed ceramic tiles	Cerium	Tin, zirconium

Alternatives to REE in some applications. (Gupta and Krishnamurthy, 2005).

Antimony

Sb – definitions and characteristics

Sb and Sb_2S_3 have been known since **4000 B.C.** The metal was used as coating to harden Cu and the sulfide as eyebrow paint.

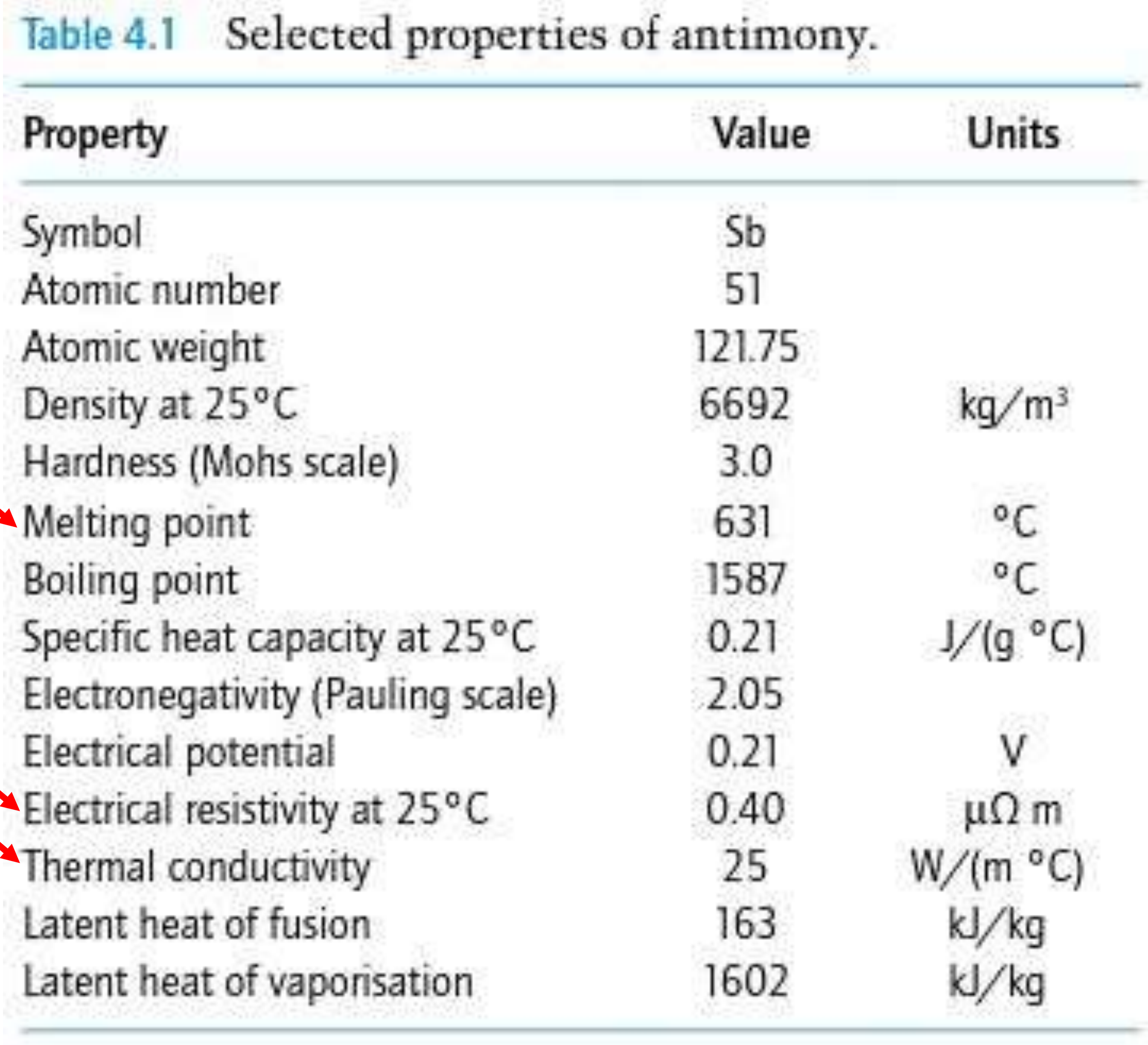


Table 4.1 Selected properties of antimony.

Property	Value	Units
Symbol	Sb	
Atomic number	51	
Atomic weight	121.75	
Density at 25°C	6692	kg/m^3
Hardness (Mohs scale)	3.0	
Melting point	631	°C
Boiling point	1587	°C
Specific heat capacity at 25°C	0.21	J/(g °C)
Electronegativity (Pauling scale)	2.05	
Electrical potential	0.21	V
Electrical resistivity at 25°C	0.40	μΩ m
Thermal conductivity	25	W/(m °C)
Latent heat of fusion	163	kJ/kg
Latent heat of vaporisation	1602	kJ/kg

Sb – abundance in the Earth and mineralogy

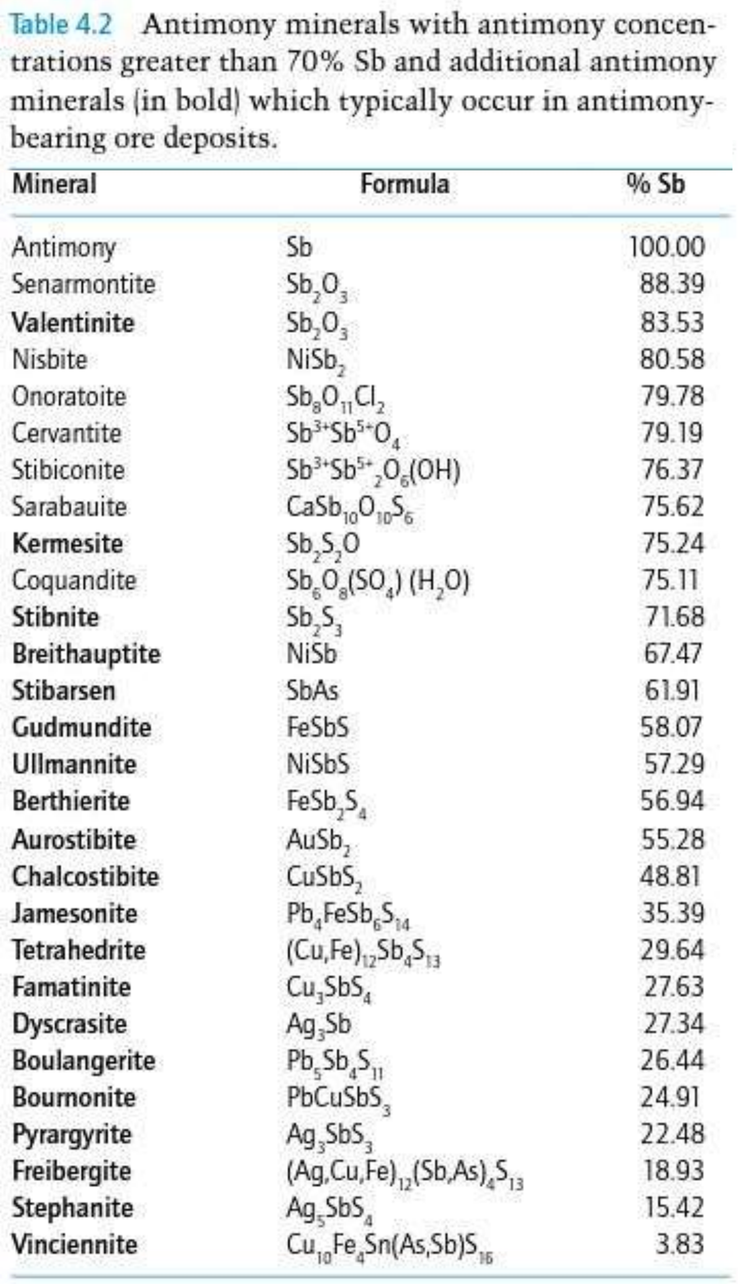


Table 4.2 Antimony minerals with antimony concentrations greater than 70% Sb and additional antimony minerals (in bold) which typically occur in antimony-bearing ore deposits.

Mineral	Formula	% Sb
Antimony	Sb	100.00
Senarmontite	Sb_2O_3	88.39
Valentinite	Sb_2O_3	83.53
Nisbite	$NiSb_2$	80.58
Onoratoite	$Sb_8O_{11}Cl_2$	79.78
Cervantite	$Sb^{3+}Sb^{5+}O_4$	79.19
Stibiconite	$Sb^{3+}Sb^{5+}{}_2O_6(OH)$	76.37
Sarabauite	$CaSb_{10}O_{10}S_6$	75.62
Kermesite	Sb_2S_2O	75.24
Coquandite	$Sb_6O_8(SO_4)(H_2O)$	75.11
Stibnite	Sb_2S_3	71.68
Breithauptite	$NiSb$	67.47
Stibarsen	$SbAs$	61.91
Gudmundite	$FeSbS$	58.07
Ullmannite	$NiSbS$	57.29
Berthierite	$FeSb_2S_4$	56.94
Aurostibite	$AuSb_2$	55.28
Chalcostibite	$CuSbS_2$	48.81
Jamesonite	$Pb_4FeSb_6S_{14}$	35.39
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	29.64
Famatinite	Cu_3SbS_4	27.63
Dyscrasite	Ag_3Sb	27.34
Boulangerite	$Pb_5Sb_4S_{11}$	26.44
Bournonite	$PbCuSbS_3$	24.91
Pyrargyrite	Ag_3SbS_3	22.48
Freibergite	$(Ag,Cu,Fe)_{12}(Sb,As)_4S_{13}$	18.93
Stephanite	Ag_5SbS_4	15.42
Vinciennite	$Cu_{10}Fe_4Sn(As,Sb)S_{16}$	3.83

- Sb has **strong affinity to S** and metals like Cu, Pb and Ag. Moderately siderophile, moderately incompatible and lithophile.

- “Antimony” is derived from the Greek words “*anti*” and “*monos*” (“not alone”).

- Sb is a lustrous silvery white, **brittle**, crystalline semi-metal (**metalloid)** with **poor conductivity of electricity and heat**.

- Sb^{5+}, Sb^{3+}, Sb^0 and Sb^{3-}

- **Clarke 0.2 ppm**, basalts vary from 0.02 ppm and 0.8 ppm, seawater 0.15 ppb.

- Sb substitutes for Bi, Pb, As and S in a variety of ore minerals. Close mineralogical association with **Ag** and **Au** deposits.

Antimonite

Sb – major deposit classes

- Sb occurs in several different types of ore deposits of **all ages**. Sb deposits are commonly associated with **active continental margins** and **orogenic belts** with **steep geothermal gradients**.

- Most of Sb deposits are of **hydrothermal origin**. Three main Sb deposits can be distinguished, based on fluid generation and metal source:

  1. Low-T hydrothermal (**epithermal**) in shallow crustal environments associated with **magmatic fluids** (calc-alkaline to peralkaline, porphyritic felsic to intermediate volcanic and intrusive, often in a volcanic cauldron setting).
  2. **Metamorphogenic** hydrothermal origin in consolidated crustal environments
  3. **Reduced intrusion-related Au systems**.

- Sb deposits may also be distinguished by their metal and mineralogical composition:
  - Simple **stibnite** (+ Au) deposits;
  - Complex **polymetallic deposits** of the "**epithermal suite**": Au, Ag, Te, Se, Hg, As, Sb, Tl and, locally, base metals (Cu, Pb, Bi, Zn).

Sb – major deposit classes

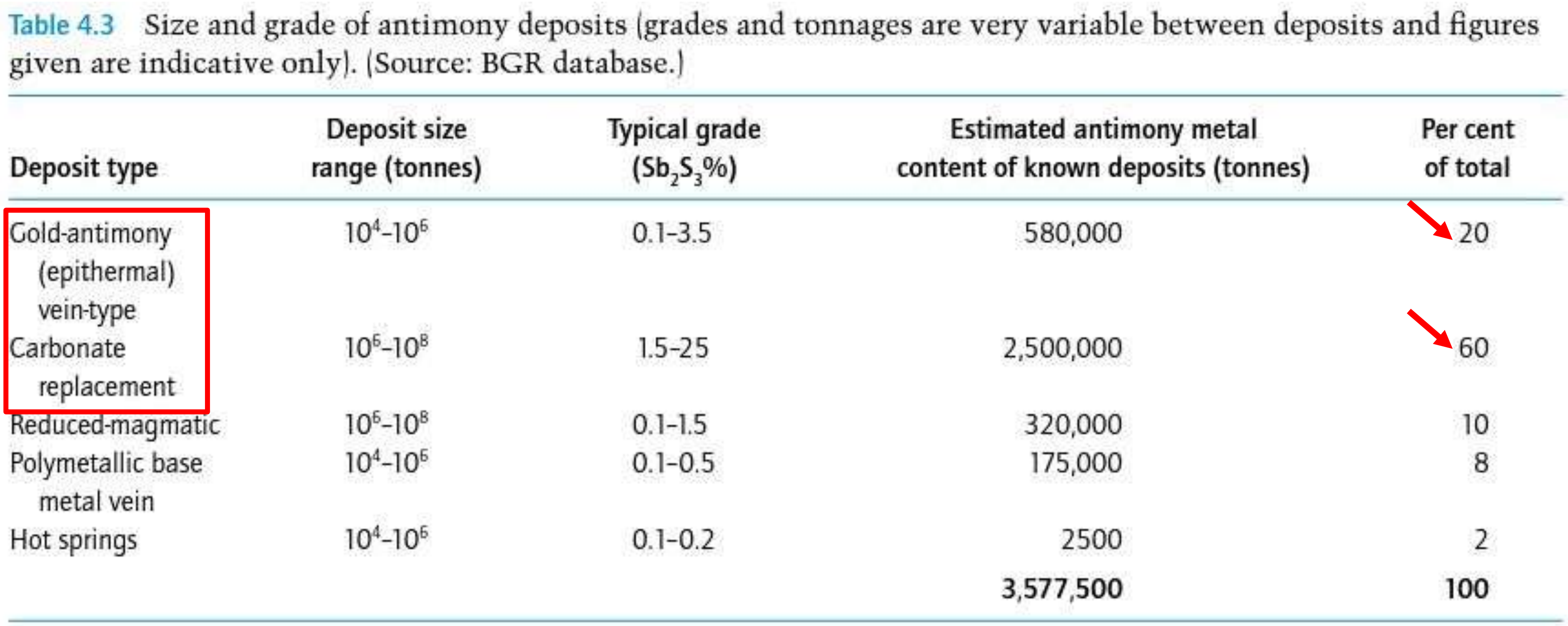
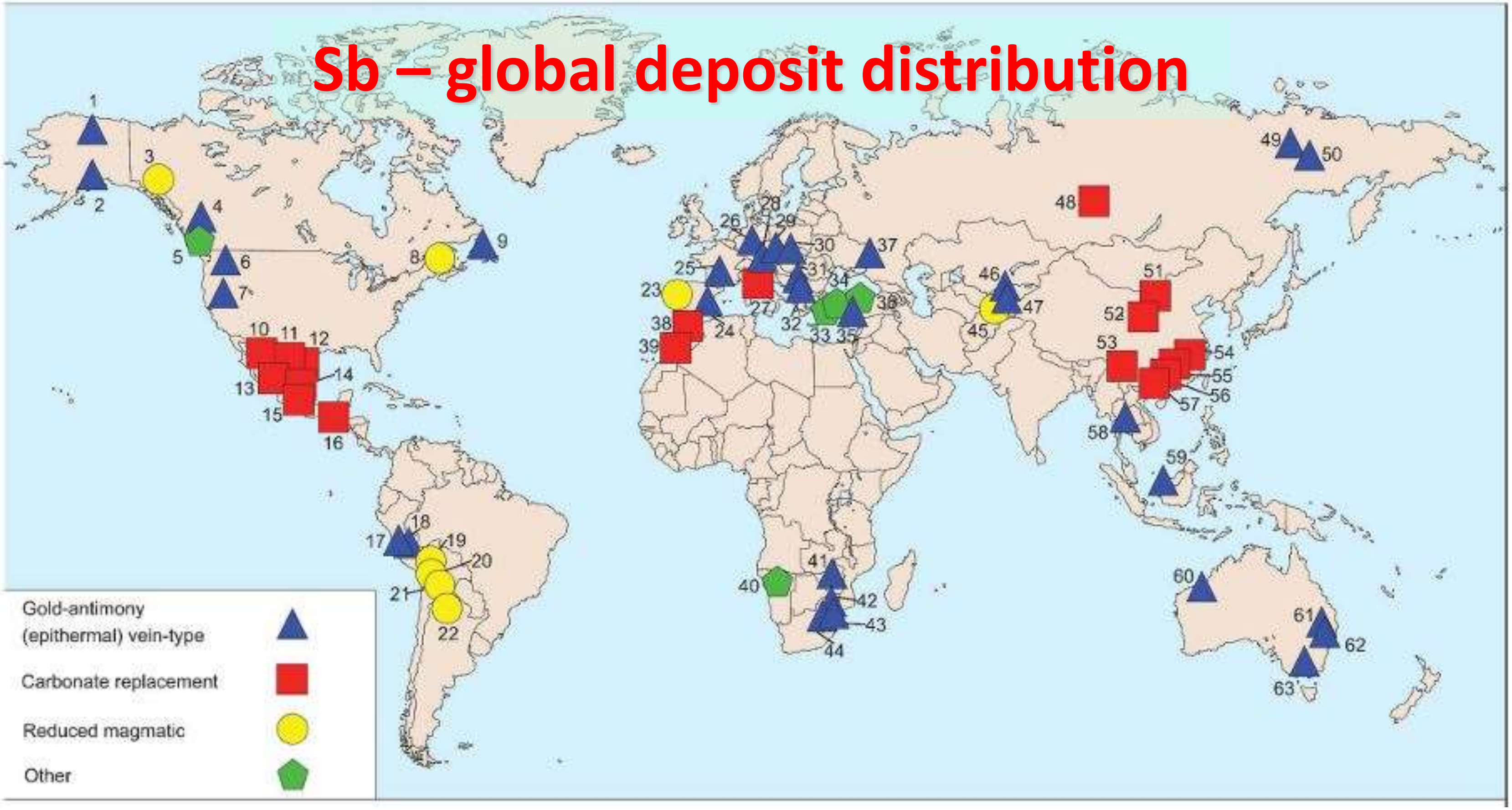


Table 4.3 Size and grade of antimony deposits (grades and tonnages are very variable between deposits and figures given are indicative only). (Source: BGR database.)

Deposit type	**Deposit size range (tonnes)**	**Typical grade (Sb_2S_3%)**	**Estimated antimony metal content of known deposits (tonnes)**	**Per cent of total**
Gold-antimony (epithermal) vein-type	10^4–10^6	0.1–3.5	580,000	20
Carbonate replacement	10^6–10^8	1.5–25	2,500,000	60
Reduced-magmatic	10^6–10^8	0.1–1.5	320,000	10
Polymetallic base metal vein	10^4–10^6	0.1–0.5	175,000	8
Hot springs	10^4–10^6	0.1–0.2	2500	2
			3,577,500	**100**

Sb – global deposit distribution



1 Workman's Bench, Nolan Creek
2 Eagle Creek
3 Becker-Cochran
4 Morris
5 Sullivan
6 Coeur d'Alene district
7 Fencemaker
8 Belledune/Lake George
9 Beaver Brook
10 Sonora district
11 Coahuila district
12 Nuevo Leon district
13 Zacatecas district
14 San Luis Potosi district
15 Queretaro district
16 Ixtahuacan (3 deposits)
17 Minera Halcon de Gorgor
18 Cobriza, La Oroya
19 Lipichi district (>10 deposits)
20 San Jose, Oruro district
21 Potosi department (>20 deposits)
22 Pabellon
23 Alto do Sobrido
24 San Antonio
25 Montagne Noi
26 Germany (3 deposits)
27 Manciano area
28 Schlaining, Burgenland
29 Krasna Hora, Bohemia
30 Slovakia (2 deposits)
31 Kostajnik-Krupanj district
32 Allchar (Alsar) district
33 Izmir Province
34 Kütahya Province
35 Nigde Province
36 Tokat Province
37 Nikitovaka
38 Beni-Msala
39 Tourtit
40 Tsumeb
41 Kwekwe district
42 Consolidated Murchison
43 Morning Mist, Barberton
44 Msauli, Barberton
45 Tajikistan (3 deposits)
46 Kassan / Chauvay
47 Kadamzhay / Khaidarkan
48 Olimpiada
49 Sentachan
50 Sarylakh
51 Changbaishan-Yinshan-Tianshan belt (10 deposits)
52 Quinling-Kunlunshan belt (>50 deposits)
53 Western Yunnan Tibet belt (10 deposits)
54 South China belt
55 South China belt (ca. 500 deposits)
56 South China belt
57 South China belt
58 Thailand (5 deposits)
59 Bau district, Sarawak
60 Blue Spec, Western Australia
61 Hillgrove, New South Wales
62 New South Wales (3 deposits)
63 Costerfield, Victoria

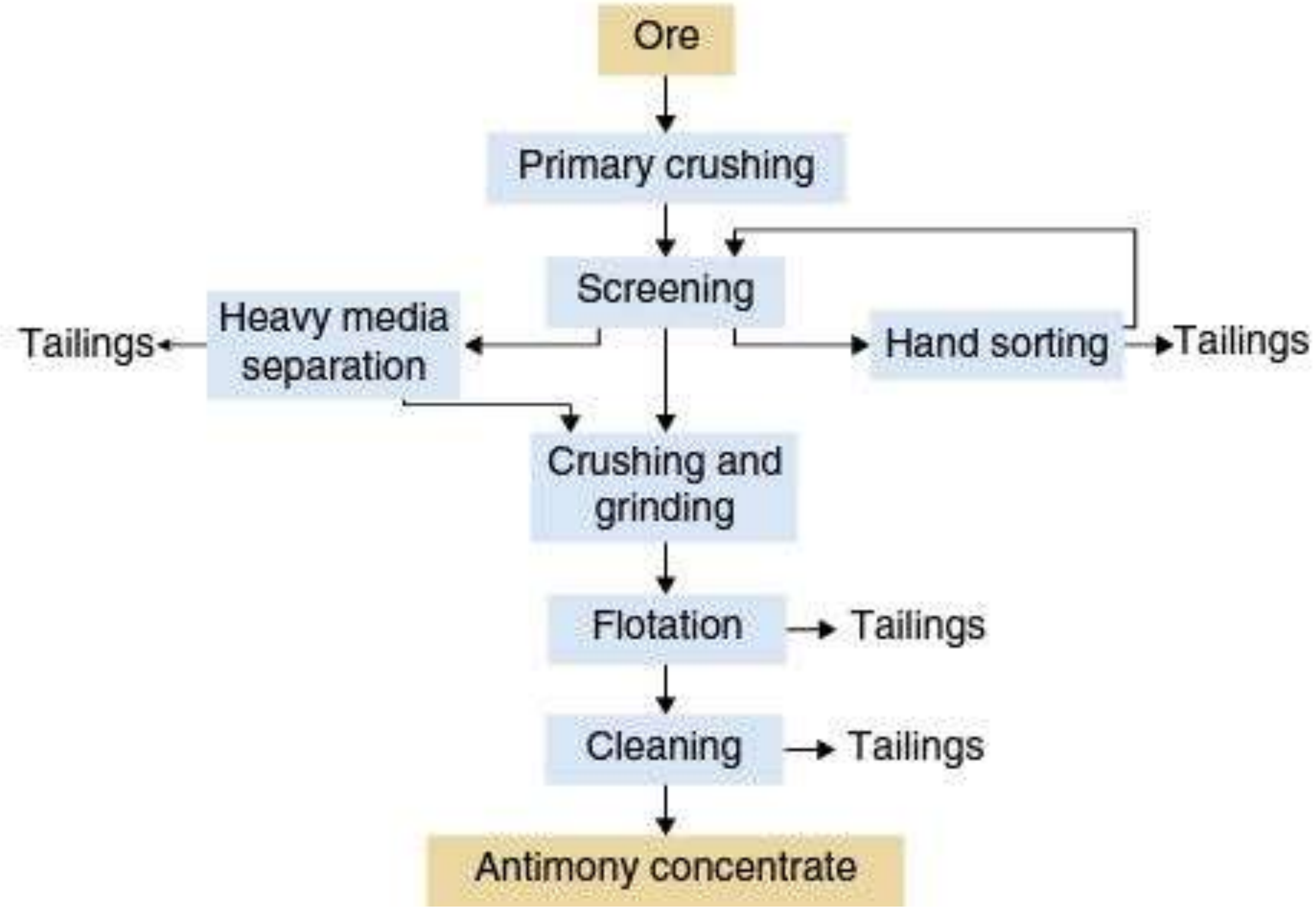
Figure 4.2 The global distribution of antimony mines, deposits and major occurrences. (Polymetallic base-metal vein deposits are not shown separately.) Some of the symbols on the map represent a single important deposit or resource, while others represent a cluster of deposits in one area or region. Antimony is also known to occur in Algeria, Bosnia and Herzegovina, Brazil, Burma (Myanmar), Ecuador, Greece, Honduras, Japan, Kazakhstan, New Zealand and Pakistan.

Sb – extraction methods and processing

- **Mining:** China, Bolivia. South Africa, Russia, Tajikistan, Turkey and Australia. Sb mining is dominated by few **stibnite-rich** deposits, with possible by-products including Au, Ag, W and Hg. **Underground mining** (shrinkage stoping) and **open pit**.

- **Ore processing**: from hand sorting to advanced mineral processing. The mineral processing stages generally include conventional crushing and grinding, followed by combined gravity concentration and flotation. At least six principal methods have been used to extract Sb from its ores, depending on the **oxidation state** and the **ore grade**.

Sb – ore processing



Ore

Primary crushing

Screening

Heavy media separation

Tailings

Hand sorting

Tailings

Crushing and grinding

Flotation

Tailings

Cleaning

Tailings

Antimony concentrate

Sb – beneficiation process

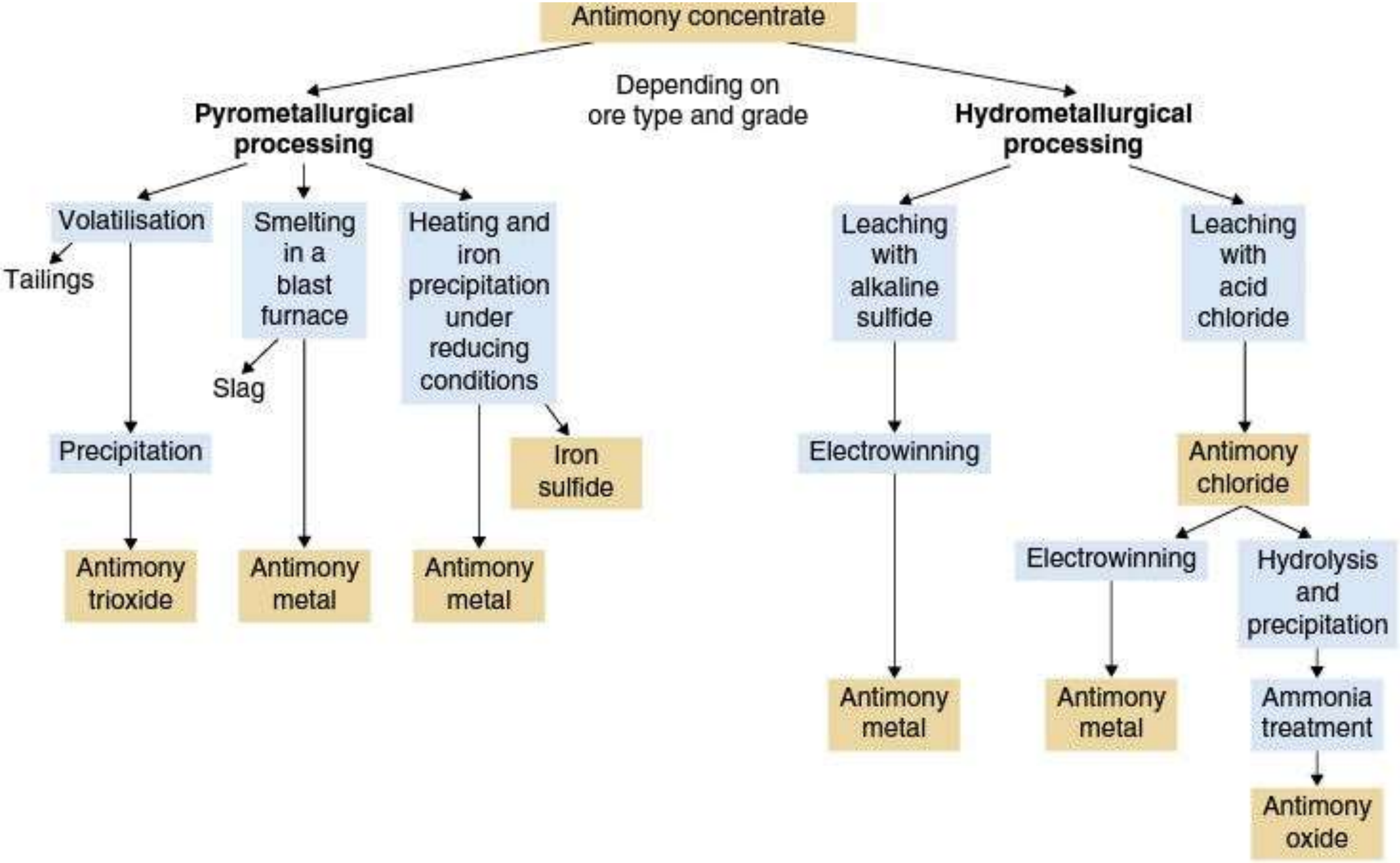


Figure 4.3 Generalised beneficiation flow diagrams, based on various ore dressing and beneficiation processes including the Xikuangshan South ore dressing plant, the Sunshine antimony process and the U.S. Antimony Corp. process. (Modified from Anderson (2000) and U.S. Antimony Corporation (2011).)

Sb – specifications and uses

- **low melting point** enhancing workability at low T;
- **stability** in air at room T and in water up to 250 °C;
- **resistance to most cold acids**; dissolution in some hot acids and in aqua regia;
- **incompatibility with strong oxidizing agents** (Cl, F);
- **high density** (6.69 g/cm^3), low hardness, brittleness;
- two allotropic forms of Sb: stable **metallic** and **amorphous** grey;
- **low electrical** and **thermal conductivity**;
- **expansion on freezing**, like Si, Bi, Ga and Ge.

USES

- **Early uses**: cast metal printing, mirrors, bell metal, pigments, bearing metal, medical and veterinary purposes (parasitic diseases).
- **Sb_2O_3** (ATO) used in **flame retardants** and **PET**;
- **$NaSbO_3$** used mainly in **cathode ray tube glass**;
- **Sb** (primary metal) used mainly in **Pb-acid batteries**;
- **Antimonial lead**, mainly recycled from and re-used in Pb-acid batteries.
- **Very high purity Sb**: **semiconductor industry**, diodes, infrared detectors.

Sb – uses and consumption

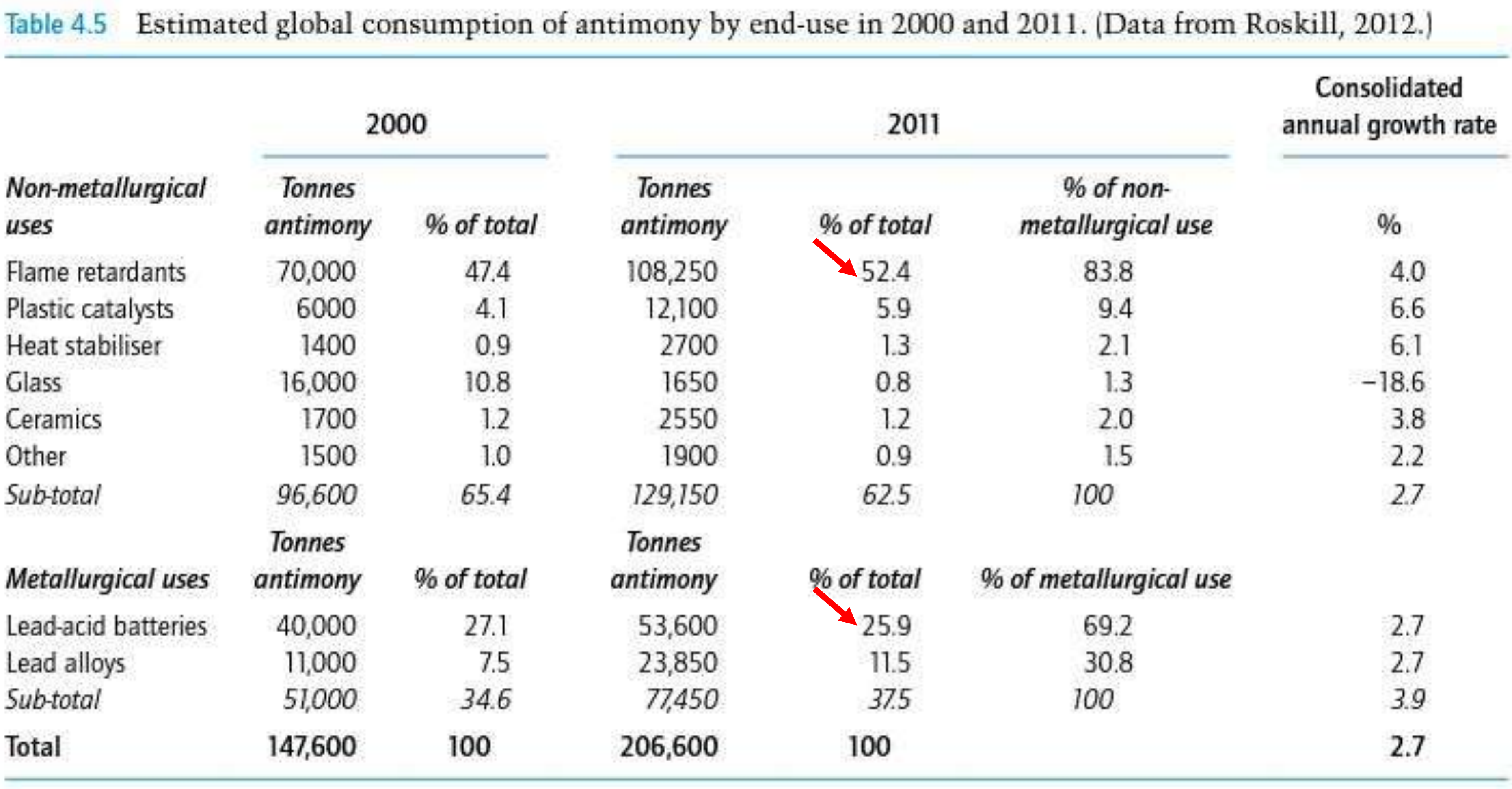


Table 4.5 Estimated global consumption of antimony by end-use in 2000 and 2011. (Data from Roskill, 2012.)

	2000		2011			Consolidated annual growth rate
Non-metallurgical uses	*Tonnes antimony*	*% of total*	*Tonnes antimony*	*% of total*	*% of non-metallurgical use*	%
Flame retardants	70,000	47.4	108,250	52.4	83.8	4.0
Plastic catalysts	6000	4.1	12,100	5.9	9.4	6.6
Heat stabiliser	1400	0.9	2700	1.3	2.1	6.1
Glass	16,000	10.8	1650	0.8	1.3	−18.6
Ceramics	1700	1.2	2550	1.2	2.0	3.8
Other	1500	1.0	1900	0.9	1.5	2.2
Sub-total	*96,600*	*65.4*	*129,150*	*62.5*	*100*	*2.7*
Metallurgical uses	*Tonnes antimony*	*% of total*	*Tonnes antimony*	*% of total*	*% of metallurgical use*	
Lead-acid batteries	40,000	27.1	53,600	25.9	69.2	2.7
Lead alloys	11,000	7.5	23,850	11.5	30.8	2.7
Sub-total	*51,000*	*34.6*	*77,450*	*37.5*	*100*	*3.9*
Total	**147,600**	**100**	**206,600**	**100**		**2.7**

Sb – recycling and substitution

- Recycling
  - For most products, such as **fire retardants**, Sb compounds cannot be recycled.
  - Most secondary Sb is obtained from recycled **Pb-acid batteries** (0.6 – 1.5 % Sb).
  - Recovery from small-arms ammunition, semiconductors, bearings and solders cannot be recycled.
- Substitution
  - **Fire-retardant materials**: alumina trihydrate, Mg hydroxide, Ca carbonate, Zn borate, etc. However, their performance is inferior to ATO.
  - **Plastic catalysts and stabilizers**: Ba, Cd, Ca, Ge, Pb, Sn, Ti and Zn lead to increased production costs.
  - **Pb-acid batteries**: Pb-Ca-Sn alloy.

Sb – resources and reserves

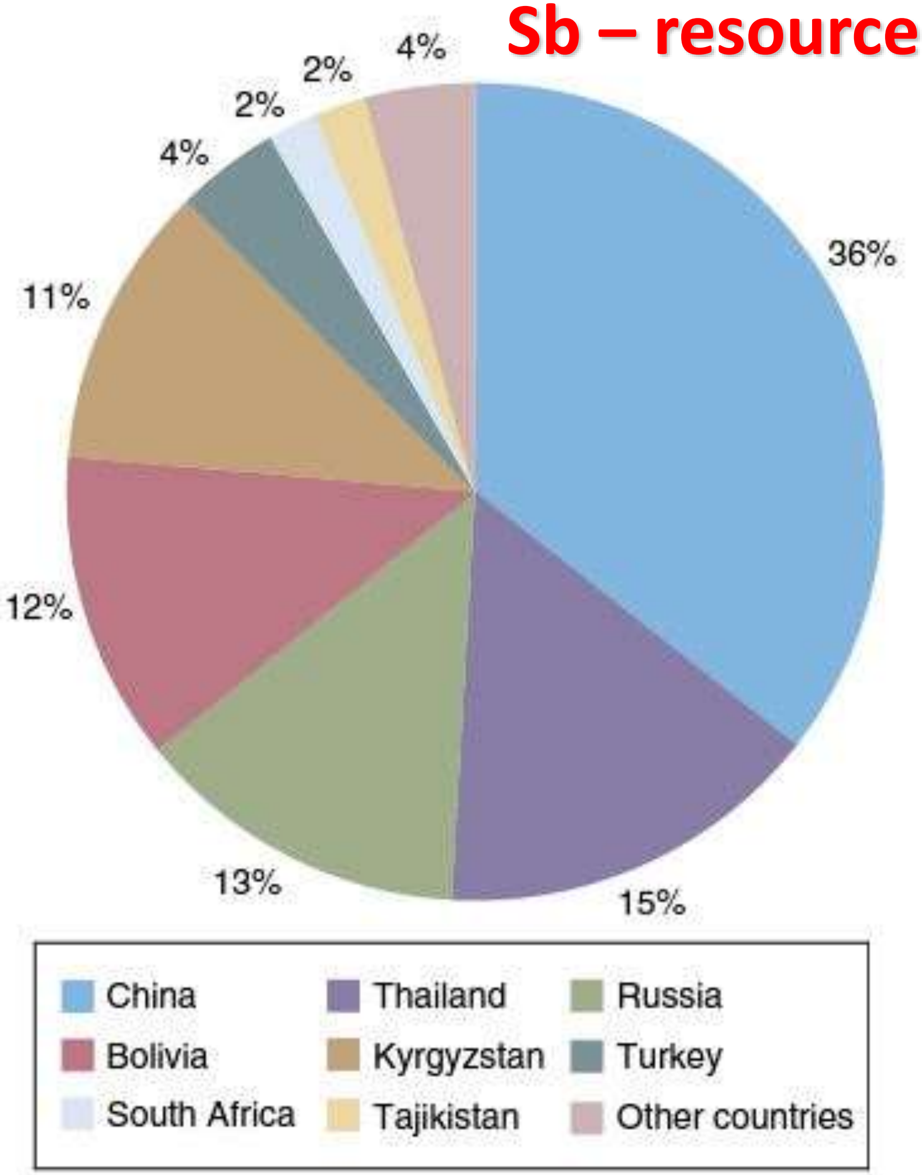


Figure 4.4 The distribution of world antimony reserves in 2011. (Data from: USGS, 2012; Roskill, 2011; Village Main Reef Ltd, 2012.)

- **Global Sb reserves**: 3.4 Mt (2011).
- **China** is the largest Sb producer.
- USGS estimate of global Sb 1.8 Mt.
- Most current projects are focusing on **epithermal** and **orogenic hydrothermal** targets.

Sb – world mine production and prices

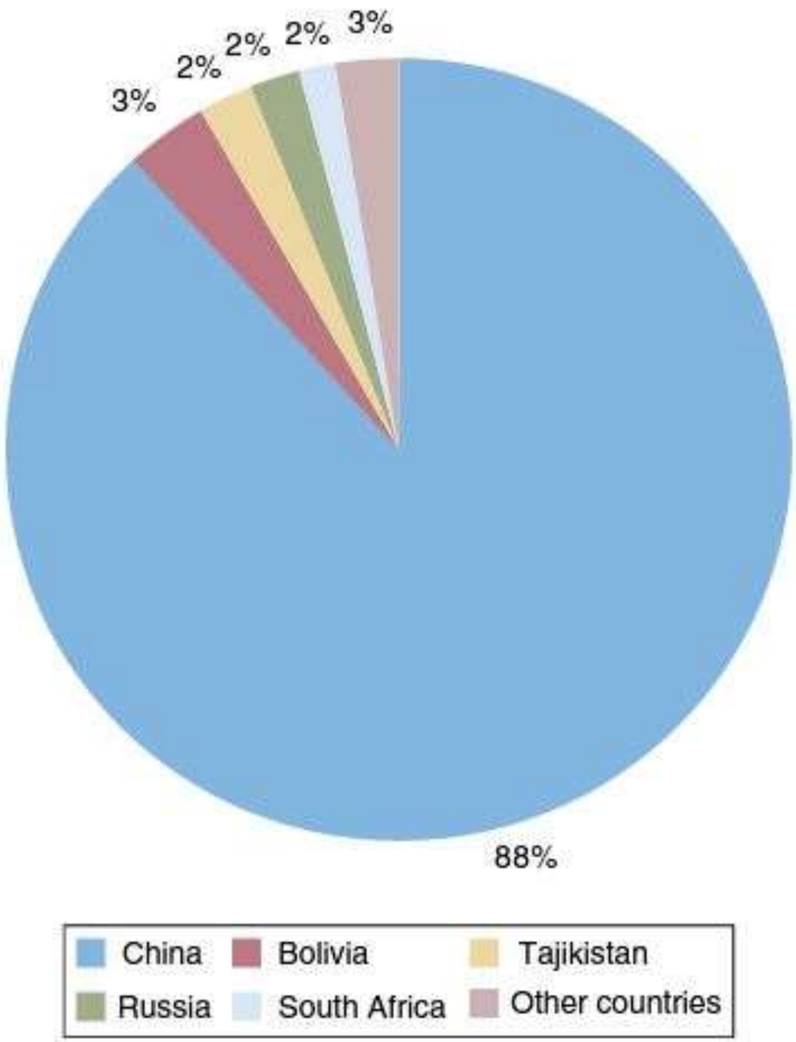


Figure 4.6 World antimony mine production in 2010, by country. (Data from British Geological Survey, 2012.)

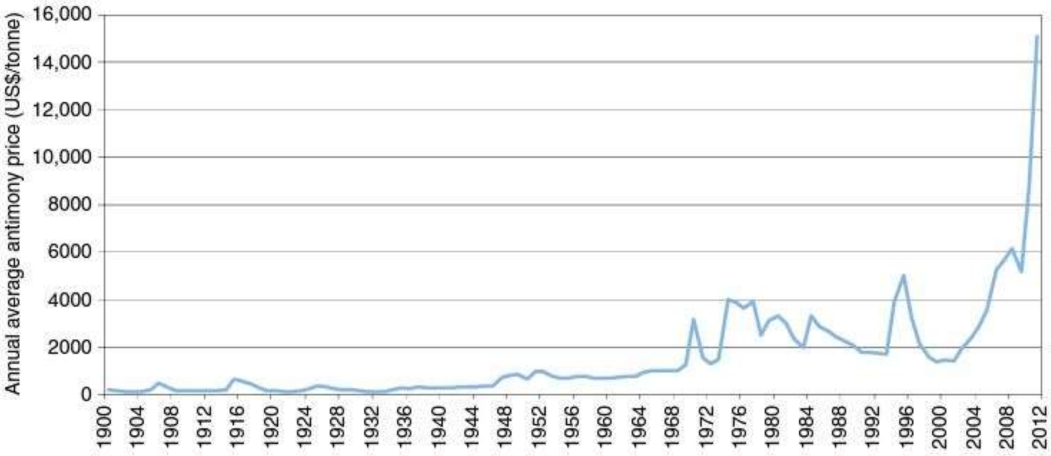


Figure 4.8 Annual average antimony prices between 1900 and 2011. (Data from BGR database.)

Sb – environmental issues

- Sb is **widely dispersed in the environment** as a result of natural processes (e.g. volcanic eruptions and erosion of Sb-bearing rocks and minerals).

- Sb is found in very low concentrations in soils, waters and air. It occurs mainly as **Sb(III)** and **Sb(V)** in environmental, biological and geochemical samples.

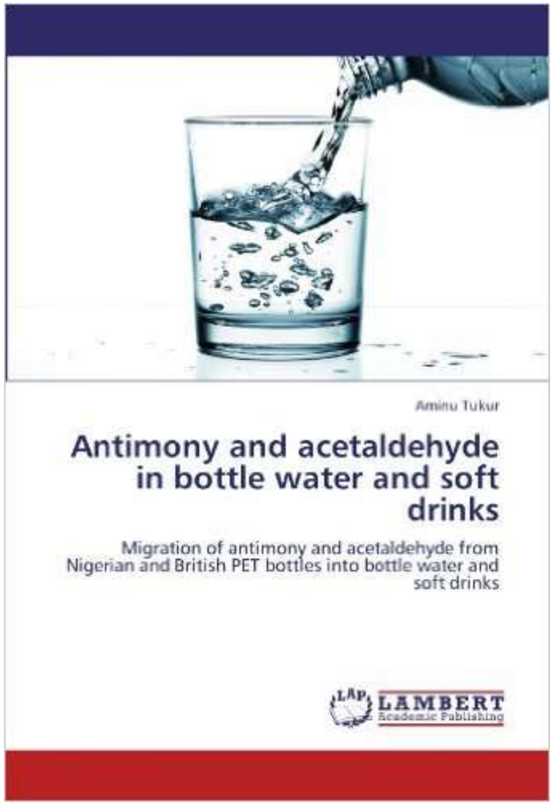
- Sb has **no known biological function**, negligible health effects (respiratory irritation, dermatitis, pneumoconiosis, gastrointestinal symptoms).

- **Sb trioxide** (ATO) is classified as "**suspected of causing cancer via inhalation**".

- NIOSH exposure limit: **0.5 mg/m^3 40-hour TWA** working week.

Sb – outlook

The use of Sb in **flame retardants** is expected to remain its principal market in the future, although its application in the production of **PET** for plastic bottles, **synthetic textiles** and for the **vulcanization of rubber** is likely to increase. The trend for Pb-acid batteries is difficult to assess.

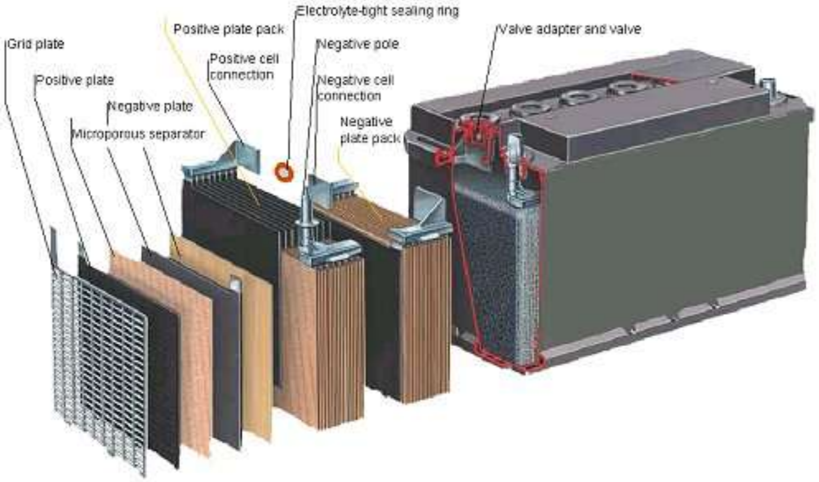


Aminu Tukur

Antimony and acetaldehyde in bottle water and soft drinks

Migration of antimony and acetaldehyde from Nigerian and British PET bottles into bottle water and soft drinks

LAP LAMBERT Academic Publishing



Beryllium

Be – definitions and characteristics

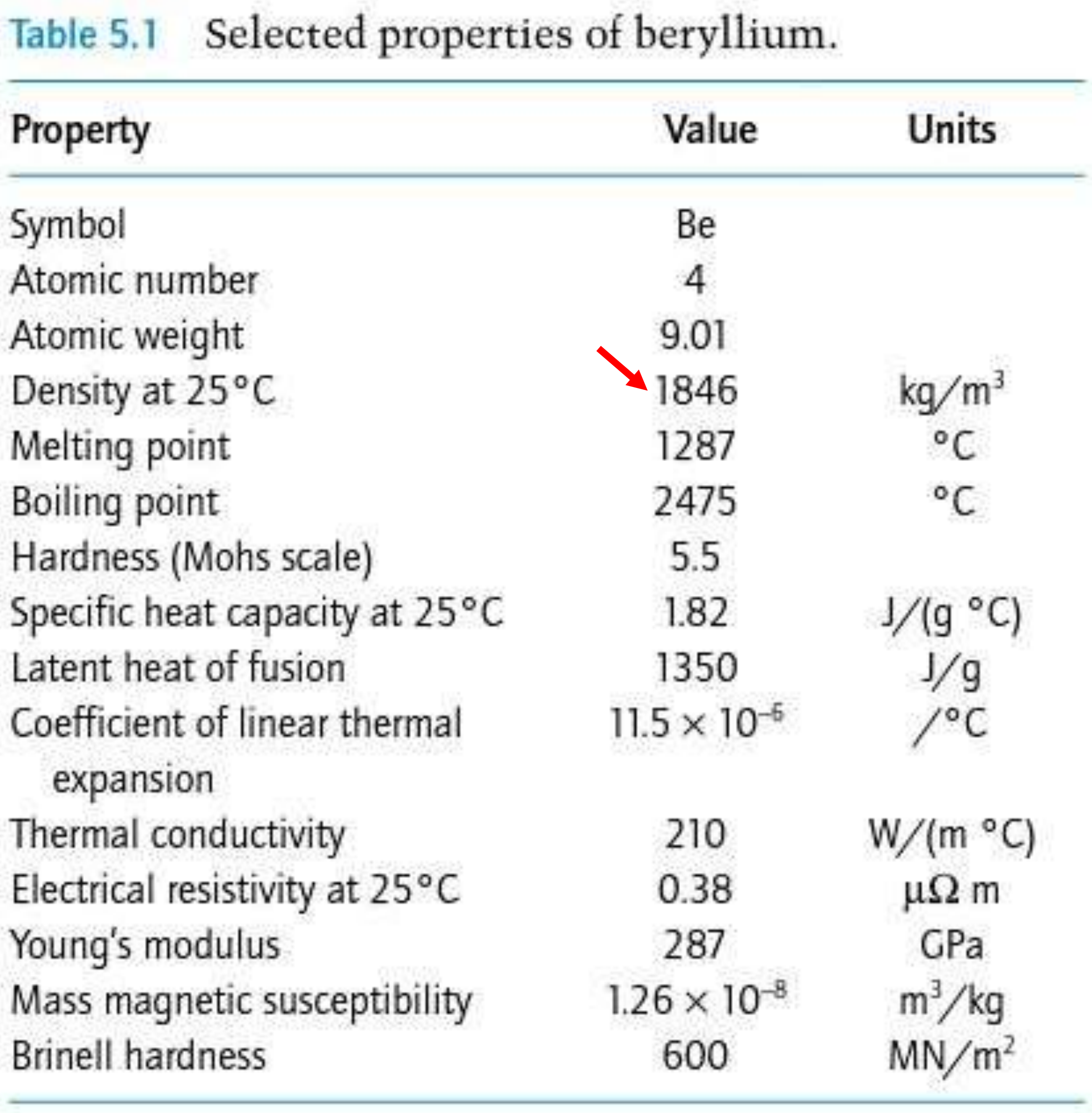


Table 5.1 Selected properties of beryllium.

Property	Value	Units
Symbol	Be	
Atomic number	4	
Atomic weight	9.01	
Density at 25°C	1846	kg/m^3
Melting point	1287	°C
Boiling point	2475	°C
Hardness (Mohs scale)	5.5	
Specific heat capacity at 25°C	1.82	J/(g °C)
Latent heat of fusion	1350	J/g
Coefficient of linear thermal expansion	11.5×10^{-6}	/°C
Thermal conductivity	210	W/(m °C)
Electrical resistivity at 25°C	0.38	μΩ m
Young's modulus	287	GPa
Mass magnetic susceptibility	1.26×10^{-8}	m^3/kg
Brinell hardness	600	MN/m^2

Be was discovered in **1797** by the French chemist Vauquelin. It was named *glucina* after its sweet-tasting salts.

The name **beryllium** was formally adopted by IUPAC in 1949.

Main physical properties: rigidity, low weight, heat-absorbing capability, dimensional stability.

Be – abundance in the Earth and mineralogy

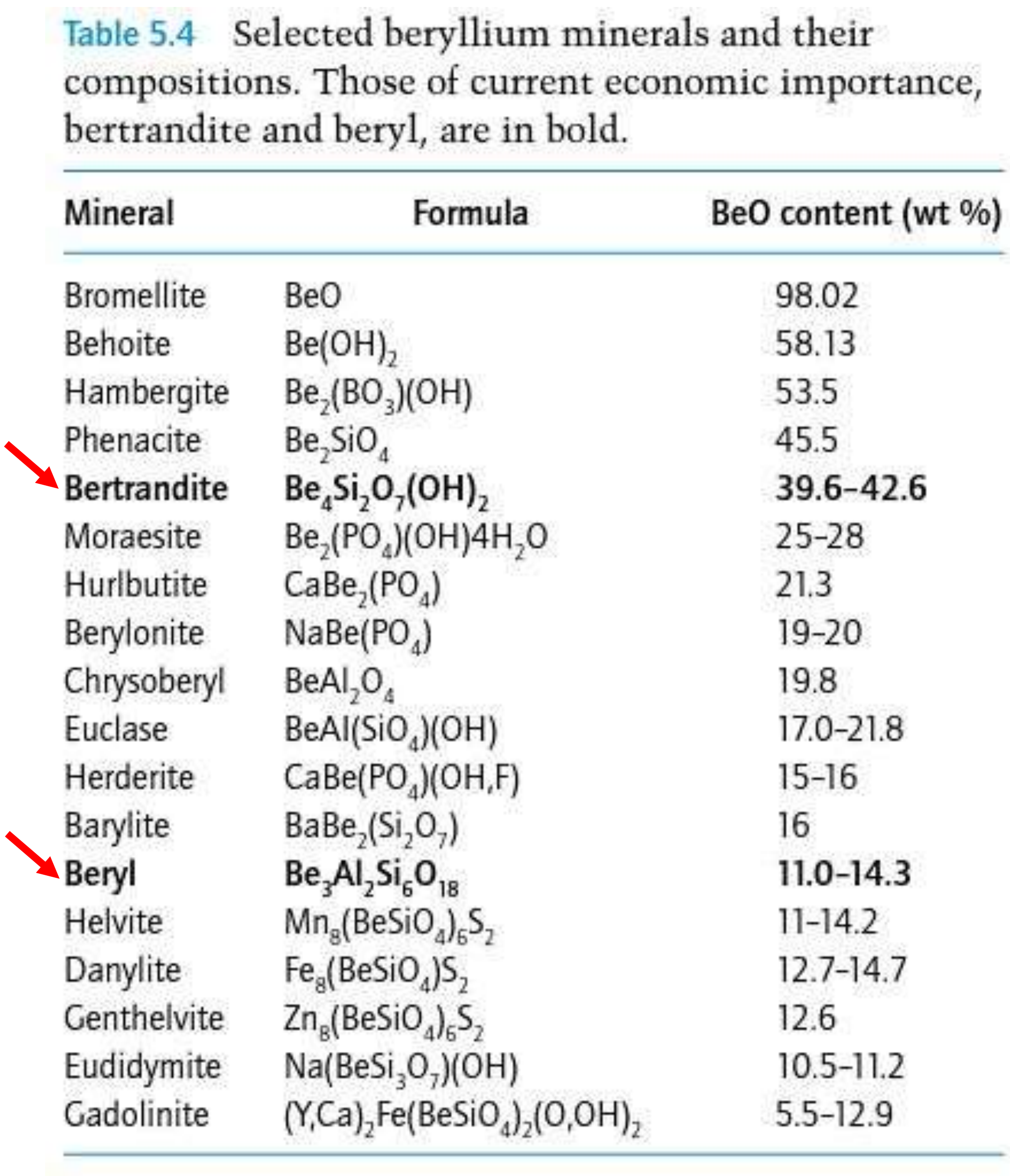


Table 5.4 Selected beryllium minerals and their compositions. Those of current economic importance, bertrandite and beryl, are in bold.

Mineral	Formula	BeO content (wt %)
Bromellite	BeO	98.02
Behoite	$Be(OH)_2$	58.13
Hambergite	$Be_2(BO_3)(OH)$	53.5
Phenacite	Be_2SiO_4	45.5
Bertrandite	**$Be_4Si_2O_7(OH)_2$**	**39.6–42.6**
Moraesite	$Be_2(PO_4)(OH)4H_2O$	25–28
Hurlbutite	$CaBe_2(PO_4)$	21.3
Berylonite	$NaBe(PO_4)$	19–20
Chrysoberyl	$BeAl_2O_4$	19.8
Euclase	$BeAl(SiO_4)(OH)$	17.0–21.8
Herderite	$CaBe(PO_4)(OH,F)$	15–16
Barylite	$BaBe_2(Si_2O_7)$	16
Beryl	**$Be_3Al_2Si_6O_{18}$**	**11.0–14.3**
Helvite	$Mn_8(BeSiO_4)_6S_2$	11–14.2
Danylite	$Fe_8(BeSiO_4)S_2$	12.7–14.7
Genthelvite	$Zn_8(BeSiO_4)_6S_2$	12.6
Eudidymite	$Na(BeSi_3O_7)(OH)$	10.5–11.2
Gadolinite	$(Y,Ca)_2Fe(BeSiO_4)_2(O,OH)_2$	5.5–12.9

- Be is a silver grey **metal**, noted for its **light weight** (density 1.846 g/cm^3).

- Be is virtually **transparent to X-rays**.

- Sound travels through Be faster than any other metal.

- When added to other metals, especially **Cu** (alloy), Be provides **controllable strengthening mechanisms** (good electrical and thermal conductivity, very low friction).

- **Non-magnetic** and **non-sparking** properties.

- **Clarke: 2.1 ppm**. Mafic and ultramafic rocks, sedimentary rocks: < 2 ppm. Felsic igneous rocks: 4 ppm; two-mica granites: 9 ppm.


Beryl


Bertrandite

Be – major deposit classes

- Be can behave as a **lithophile**, **chalcophile** and **siderophile** element, forming a variety of minerals.

- **Bertrandite** and **beryl** are the most important ore minerals.

- Potential future production may come from **phenacite** Be_2SiO_4 mining.

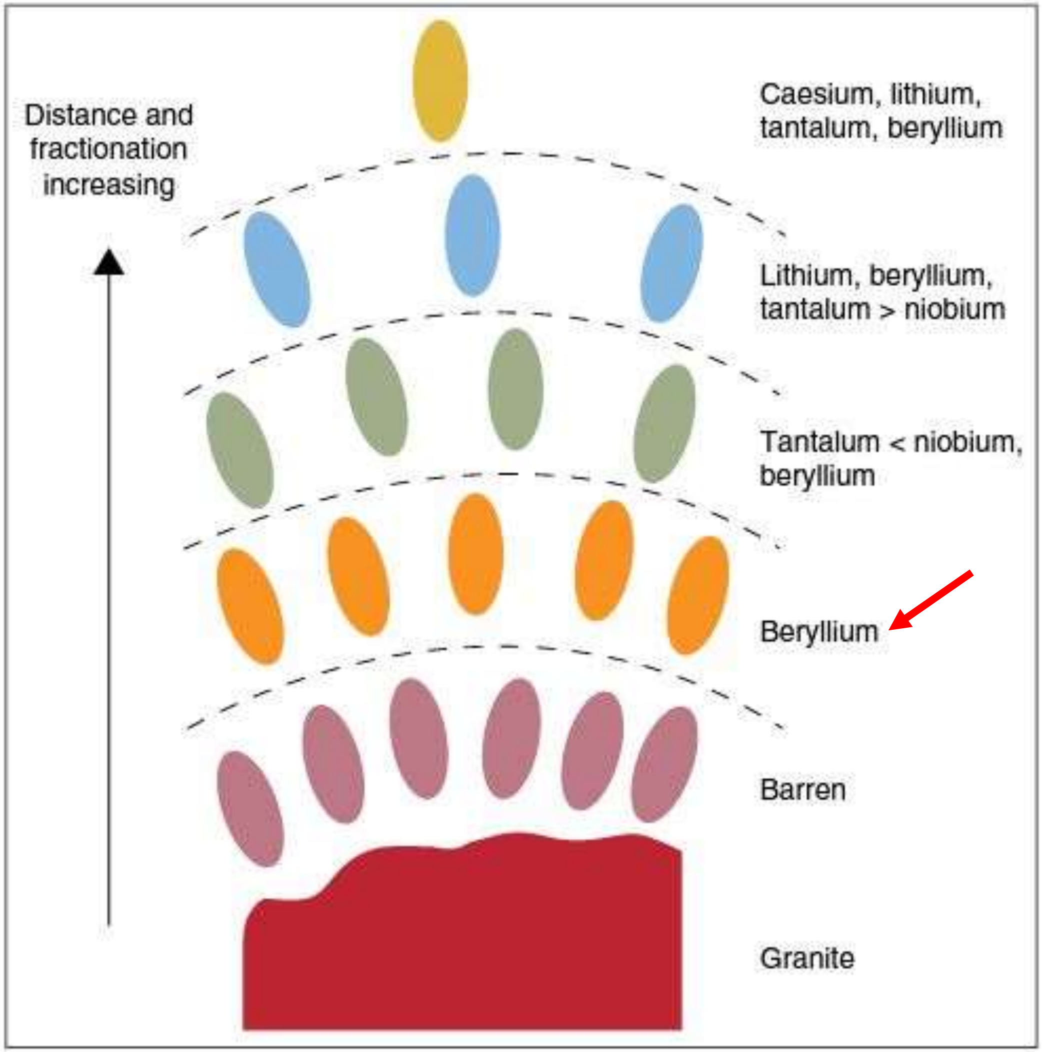
- Most commonly found in **sub-alkaline granitic pegmatitic suites**.

- Bertrandite and phenacite are found in both sub-alkaline and alkaline systems.

Two principal types of deposits:

1. **Granitic pegmatite deposits**

2. **Hydrothermal-metasomatic deposits**



Rare-element zoning in pegmatite fields. (After Trueman and Černý, 1982.)

Be – major deposit classes

Pegmatite deposits

Granitic pegmatites may be divided into two classes:

1. **Li – Cs – Ta** (**LCT**) – related to S- and I-granites (**subduction** and/or **collisional setting**), generally occurring in **swarms** → more important source of **beryl**. Be, usually in the form of beryl, makes an **early appearance** in the zoned sequence **close to the source granite intrusion**. With increasing fractionation the elements Na and Cs substitute for Be in the beryl lattice and lower the quality.

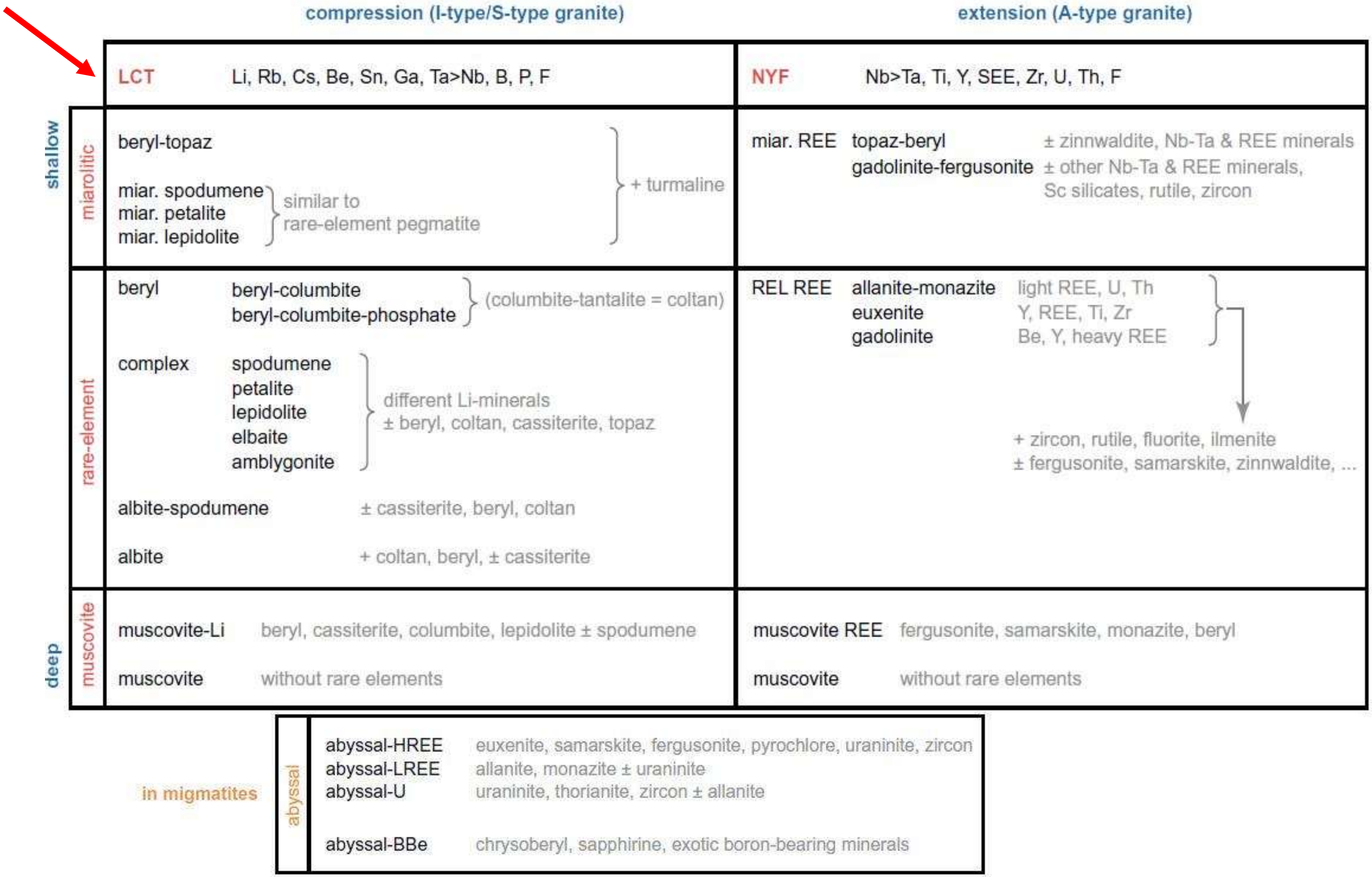
2. **Nb – Y – F** (**NYF**) - related to **extensional (anorogenic) tectonic settings**, tend to occur within **restricted areas**, **proximal** to their parental rocks. No commercial Be production is known from NYF pegmatites.

Hydrothermal deposits

- Broad category including **replacement, skarn, greisen** and **vein deposits**.

- The deposits are generally related to **felsic magmatism**.

- The **high F content** depresses the freezing point of these magmas and allows **protracted enrichment of incompatible elements**, such as Be, into the late hydrothermal phase.



		compression (I-type/S-type granite)	extension (A-type granite)
		LCT Li, Rb, Cs, Be, Sn, Ga, Ta>Nb, B, P, F	NYF Nb>Ta, Ti, Y, SEE, Zr, U, Th, F
shallow	miarolitic	beryl-topaz miar. spodumene miar. petalite miar. lepidolite similar to rare-element pegmatite + turmaline	miar. REE topaz-beryl ± zinnwaldite, Nb-Ta & REE minerals gadolinite-fergusonite ± other Nb-Ta & REE minerals, Sc silicates, rutile, zircon
	rare-element	beryl beryl-columbite beryl-columbite-phosphate (columbite-tantalite = coltan) complex spodumene petalite lepidolite elbaite amblygonite different Li-minerals ± beryl, coltan, cassiterite, topaz albite-spodumene ± cassiterite, beryl, coltan albite + coltan, beryl, ± cassiterite	REL REE allanite-monazite light REE, U, Th euxenite Y, REE, Ti, Zr gadolinite Be, Y, heavy REE + zircon, rutile, fluorite, ilmenite ± fergusonite, samarskite, zinnwaldite, ...
deep	muscovite	muscovite-Li beryl, cassiterite, columbite, lepidolite ± spodumene muscovite without rare elements	muscovite REE fergusonite, samarskite, monazite, beryl muscovite without rare elements
in migmatites	abyssal	abyssal-HREE euxenite, samarskite, fergusonite, pyrochlore, uraninite, zircon abyssal-LREE allanite, monazite ± uraninite abyssal-U uraninite, thorianite, zircon ± allanite abyssal-BBe chrysoberyl, sapphirine, exotic boron-bearing minerals	

Classification of pegmatites. The lithium–cesium–tantalum (LCT) and niobium–yttrium–fluorine (NYF) families follow different enrichment trends as a result of different parent granites and the tectonic setting. Depth also has an effect on mineral content. Rare elements are particularly enriched in shallow miarolitic pegmatites and in rare element pegmatites formed at medium depth. Within these pegmatite classes different types and subtypes can be distinguished. There are gradual transitions between the different types. Abyssal pegmatites are different because they are not formed as the residual melt of a granite but in situ by a low degree of melting (from Černý 1992; Černý and Ercit 2005)

Be – world deposit distribution

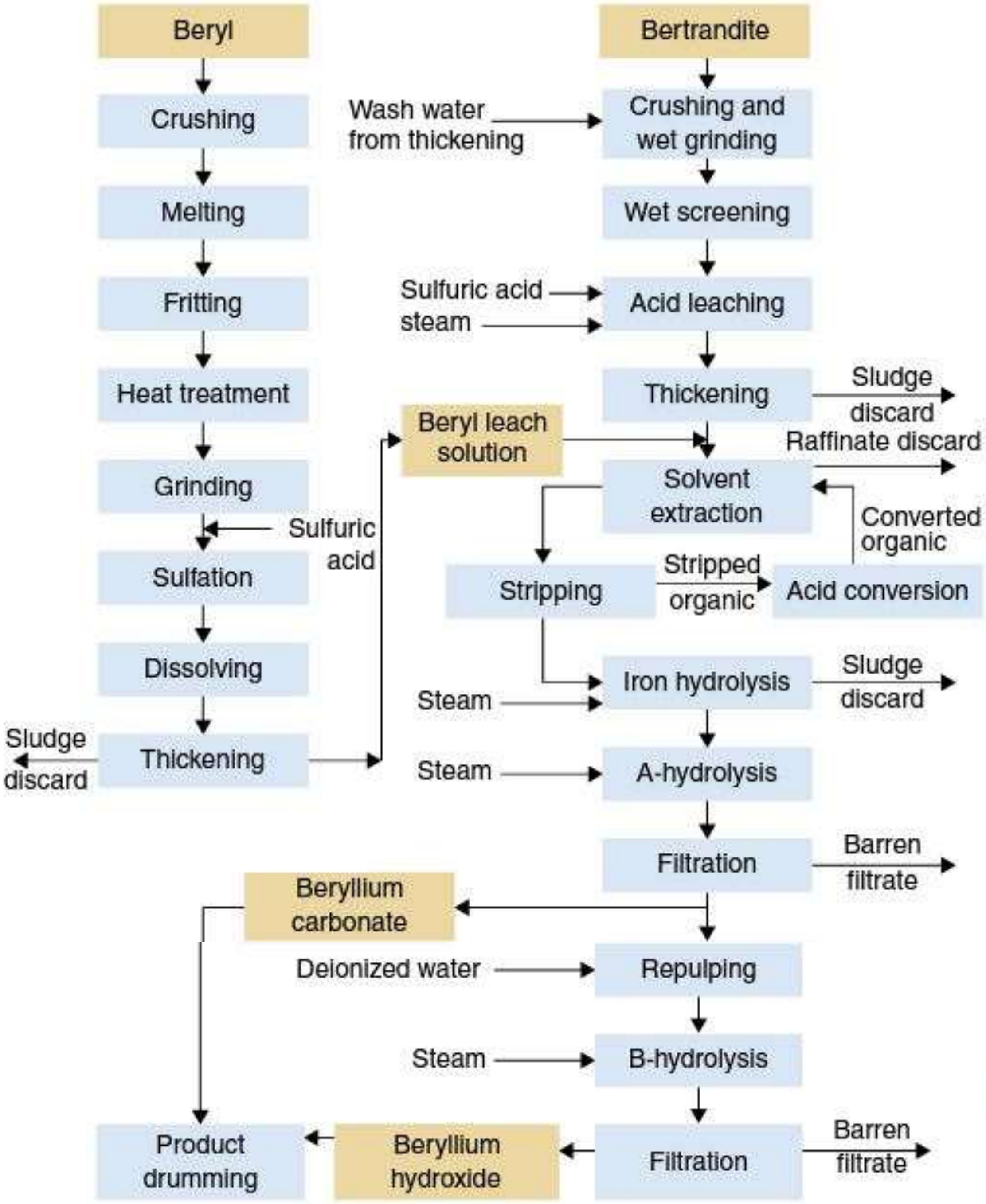
1 Lost River
2 Thor Lake
3 Moose
4 Hellroaring Creek
5 McCullough Butte
6 Mount Wheeler
7 Gold Hill
8 Spor Mountain
9 Tanco
10 Black Hills
11 Boomer
12 Iron Mountain
13 Sierra Blanca
14 Aguachile
15 Eskimo Hill
16 Strange Lake
17 Seal Lake
18 Kings Mountain
19 Muzo
20 Arequipa
21 Los Patos
22 Santa Elena, Salta
23 Quines, San Luis
24 Minas Gerais
25 Aracuai
26 Leinster
27 Gonçalo
28 Galicia
29 Echassieres
30 Varutrask
31 Elba
32 Volodarsk-Volinskiy
33 Bougoni/Kenieba
34 Issia
35 Taghouaji complex
36 Central Nigeria pegmatites
37 Rubicon
38 Bikita
39 Gravelotte
40 Marropino / Morrua
41 Anjanabonoina
42 Kibaran belt pegmatites
43 Kenticha
44 Ekaterburgskaya
45 Orenburga
46 Aqshatau
47 Kalesay
48 Laghman
49 Mingora
50 Koktokay, Xinjiang
51 Andhra Pradesh
52 Karnataka
53 Tamil Nadu
54 Yermakovskoye
55 Nerchinsk Mines
56 Huya, Pingwu, Sichuan
57 Mogok
58 Dajishan, Jiangxi
59 Wodgina
60 Greenbushes
61 Mount Cattlin

Be – extraction methods

- **Mining**
  - **Beryl** ores are extracted by **manual process** or simultaneous extraction. Beryl can be concentrated by various novel **flotation** processes.
  - **Bertrandite** ores are extracted both in open pit and underground mines.

Materion Brush open-pit mining at Spor mountain, Utah.

Be – processing: hydroxide production



Beryl

Crushing

Melting

Fritting

Heat treatment

Grinding

Sulfuric acid

Sulfation

Dissolving

Thickening

Sludge discard

Beryl leach solution

Bertrandite

Wash water from thickening

Crushing and wet grinding

Wet screening

Sulfuric acid

steam

Acid leaching

Thickening

Sludge discard

Raffinate discard

Solvent extraction

Converted organic

Stripping

Stripped organic

Acid conversion

Iron hydrolysis

Steam

Sludge discard

Steam

A-hydrolysis

Filtration

Barren filtrate

Beryllium carbonate

Deionized water

Repulping

Steam

B-hydrolysis

Filtration

Barren filtrate

Beryllium hydroxide

Product drumming

Figure 5.9 Beryllium hydroxide production from bertrandite and beryl. (Source: Materion Corp.)

Be – processing: oxide production

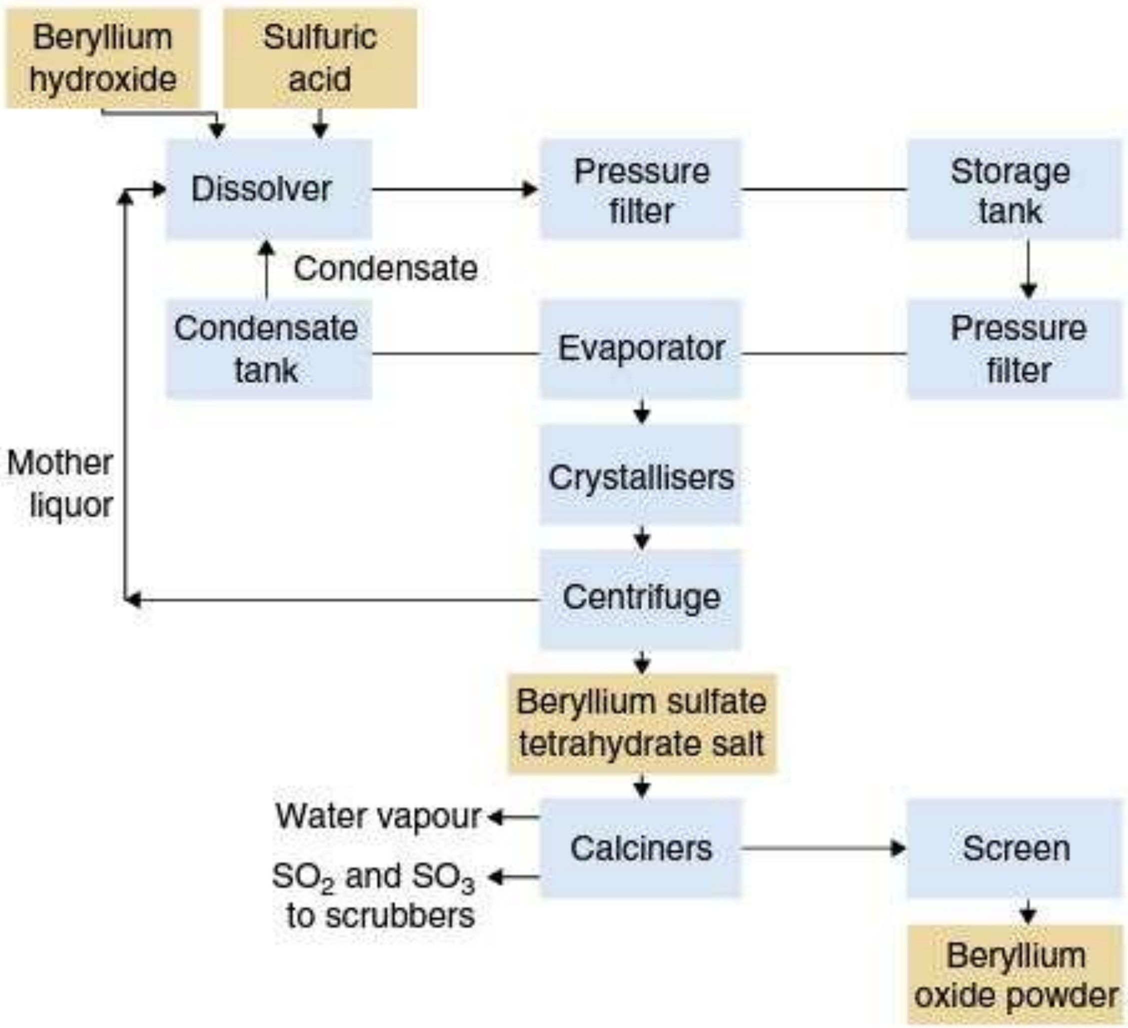
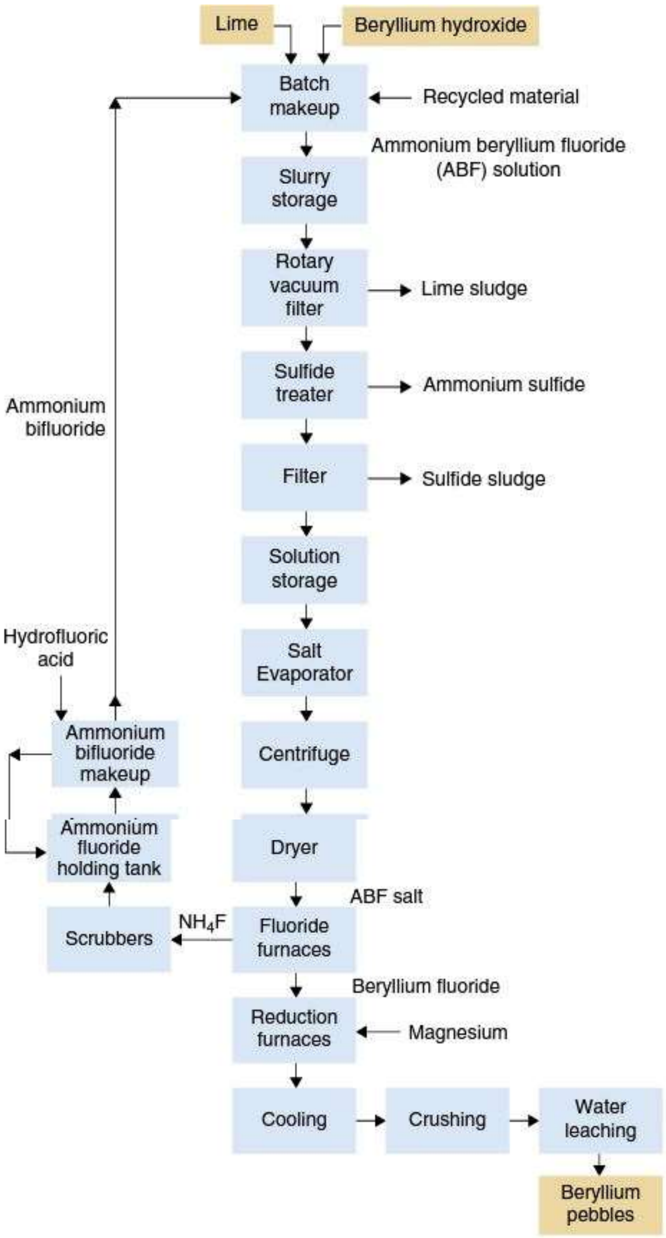


Figure 5.12 Flow sheet for production of beryllia or beryllium oxide. (Source: Materion Corp.)

Be – processing: metal production



Lime

Beryllium hydroxide

Batch makeup

Recycled material

Ammonium beryllium fluoride (ABF) solution

Slurry storage

Rotary vacuum filter

Lime sludge

Sulfide treater

Ammonium sulfide

Filter

Sulfide sludge

Solution storage

Salt Evaporator

Centrifuge

Dryer

ABF salt

Fluoride furnaces

NH_4F

Scrubbers

Ammonium fluoride holding tank

Ammonium bifluoride makeup

Hydrofluoric acid

Ammonium bifluoride

Beryllium fluoride

Reduction furnaces

Magnesium

Cooling

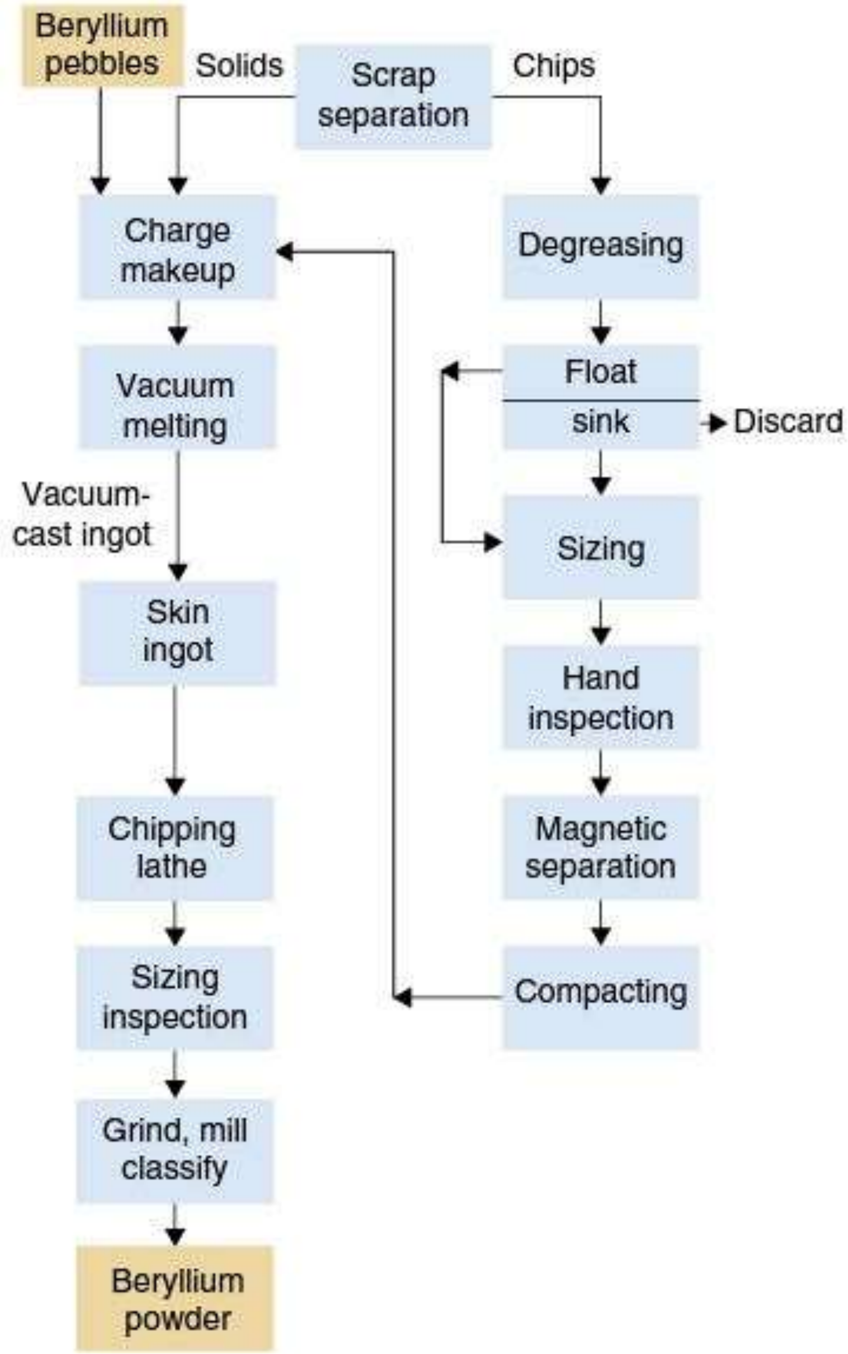
Crushing

Water leaching

Beryllium pebbles

Production of beryllium metal (Source: Materion Corp.)

Be – processing: final purification, grinding and sizing of Be powders



Beryllium pebbles

Solids

Scrap separation

Chips

Charge makeup

Vacuum melting

Vacuum-cast ingot

Skin ingot

Chipping lathe

Sizing inspection

Grind, mill classify

Beryllium powder

Degreasing

Float

sink

Discard

Sizing

Hand inspection

Magnetic separation

Compacting

Figure 5.11 Final purification, grinding and sizing of beryllium powders. This is also a starting point for beryllium recycling. (Source: Materion Corp.)

Be – specifications and uses

The three primary forms of Be used commercially are:

1. Alloys containing small amounts of Be, especially **Cu-Be** (Cu-Be alloys contain < 2% Be). Smaller Be quantities are also used to make alloys of Al and Ni → **75% Be consumption.**

USES

- **Connector terminals** for high-reliability electrical and electronic connections between circuit boards (e.g. ABS, ESP, airbag, telecommunications).
- **Relays** for industrial, domestic and automobile electrical equipment.
- **Electromagnetic radiation shielding** spring strips.
- **Diaphragms for P sensing** in aircraft altimeters, medical stethoscopes, barometers and automobile timing sensors (e.g. crankshaft, camshaft).
- **Long service-life springs** (e.g. sprinkler water-control valves).
- **Non-magnetic equipment** components used in oil and gas exploration and production.
- **Undersea cable signal amplification** "repeater" housing.
- Low-friction, high-strength aircraft **landing gear**, flap-bearing bushes.
- **Non-sparking, high-strength tools** (anesthetic gas controls, petrol refinery, etc.).
- **Plastic injection** and blow-moulding moulds.

Be – specifications and uses

2. Pure Be metal (> 99.5% and alloys containing > 60% Be) → **20% Be consumption**.

USES

- **High technology equipment** (structures to be launched into space, astronomical telescope mirrors).
- **Window for X-ray tubes and detectors**.
- **Wall-lining material** for high-T gas plasma of fusion processes.
- With the addition of **Al** (up to 62% wt.), lightweight **high-strength components of aerospace** and **electronic systems** (aerospace and munitions guidance systems).

3. Beryllia (BeO) ceramics, high electrical insulation, hardness slightly lower than diamond, thermal conductivity an order of magnitude greater than that of alumina → **5% Be consumption**.

USES

- **Electrical insulator** for heat sinks for radio-frequency and radar equipment, automotive electrical systems, laser bores and microwave waveguides.

Be – uses and consumption

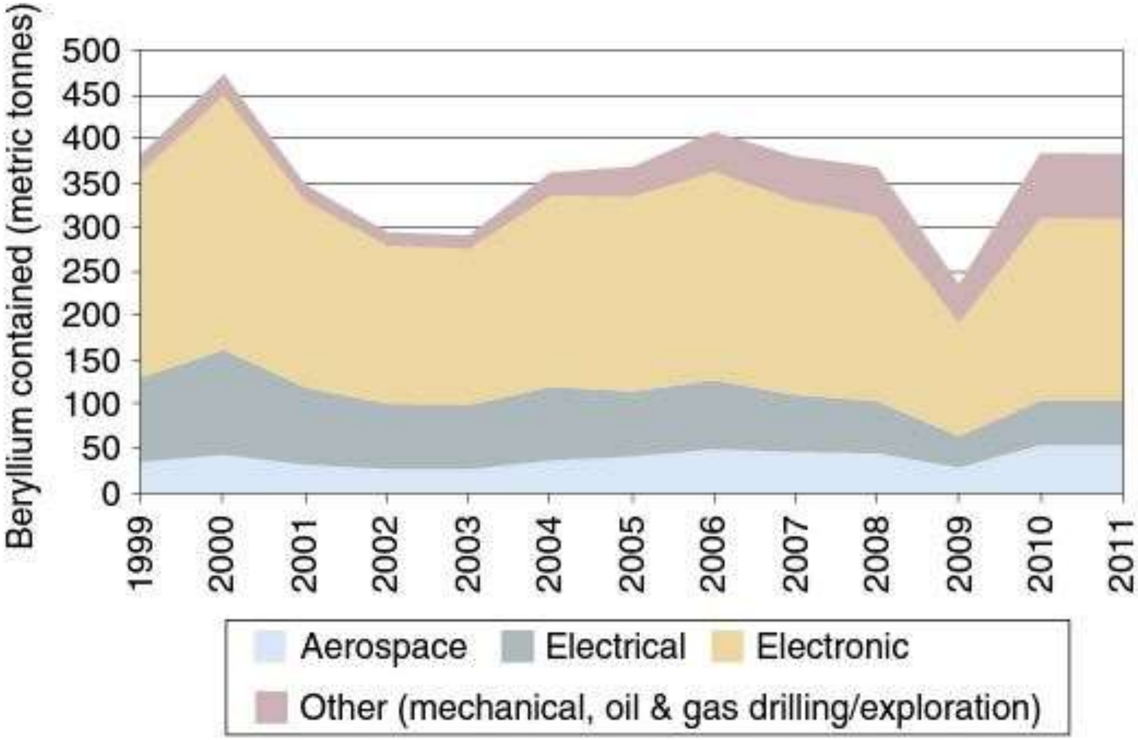


Figure 5.1 Consumption of beryllium by end-use sector, 1999–2011. (Data from BeST, 2012a.)

Be – resources

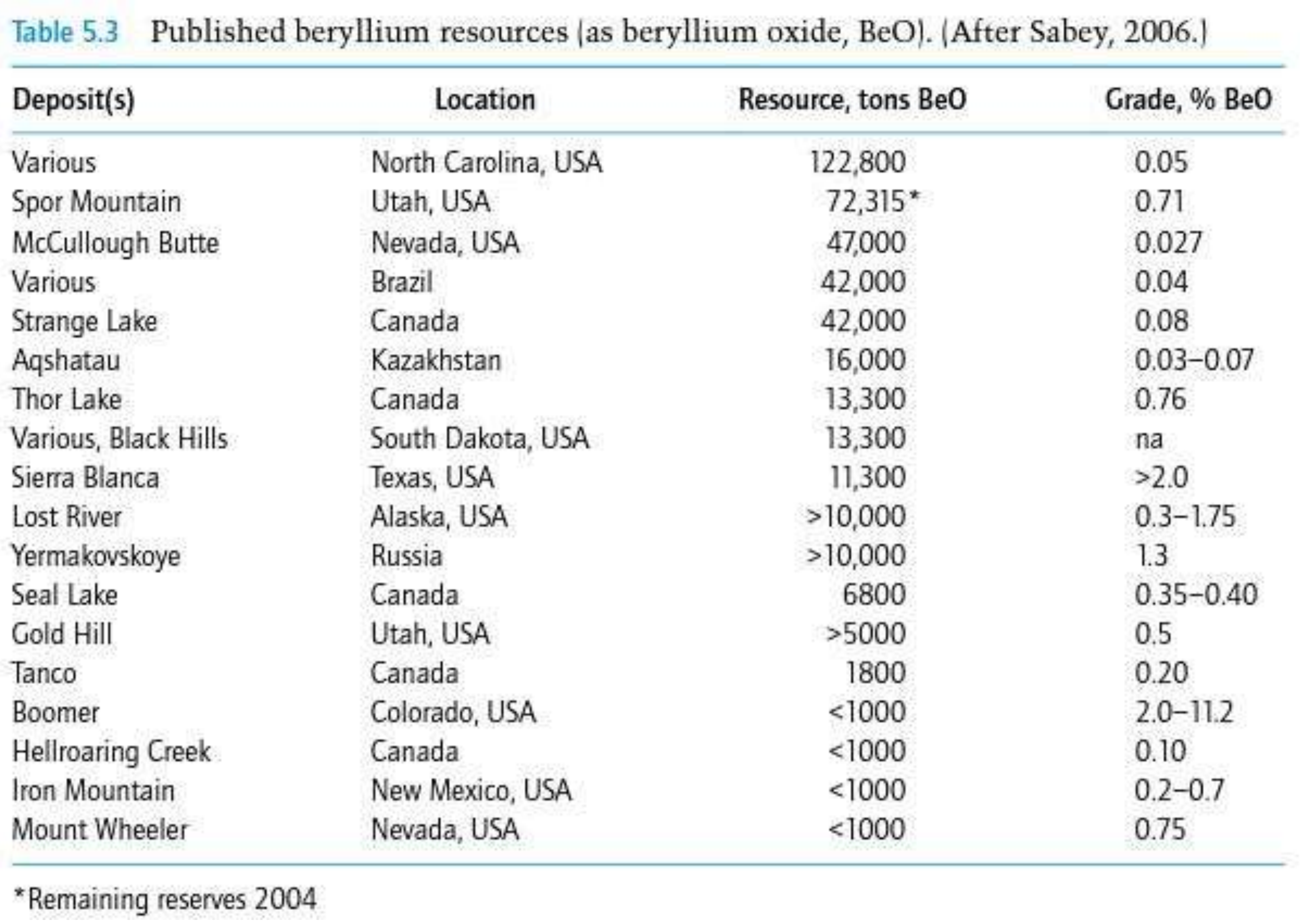


Table 5.3 Published beryllium resources (as beryllium oxide, BeO). (After Sabey, 2006.)

Deposit(s)	Location	Resource, tons BeO	Grade, % BeO
Various	North Carolina, USA	122,800	0.05
Spor Mountain	Utah, USA	72,315*	0.71
McCullough Butte	Nevada, USA	47,000	0.027
Various	Brazil	42,000	0.04
Strange Lake	Canada	42,000	0.08
Aqshatau	Kazakhstan	16,000	0.03–0.07
Thor Lake	Canada	13,300	0.76
Various, Black Hills	South Dakota, USA	13,300	na
Sierra Blanca	Texas, USA	11,300	>2.0
Lost River	Alaska, USA	>10,000	0.3–1.75
Yermakovskoye	Russia	>10,000	1.3
Seal Lake	Canada	6800	0.35–0.40
Gold Hill	Utah, USA	>5000	0.5
Tanco	Canada	1800	0.20
Boomer	Colorado, USA	<1000	2.0–11.2
Hellroaring Creek	Canada	<1000	0.10
Iron Mountain	New Mexico, USA	<1000	0.2–0.7
Mount Wheeler	Nevada, USA	<1000	0.75

*Remaining reserves 2004

Be – recycling and substitution

- **Recycling**
  - Pure Be metal components have extremely long lifetimes.

  - Some applications (space, military) do not return at all.

  - Due to its hardness, it is a difficult metal to machine.

  - Cu-Be and Ni-Be alloys are directly recycled to produce new alloys.

  - It is not economic to recover Be from Cu-Be alloys used in electronic components.

- **Substitution**
  - Substitution is difficult where its specific properties are crucial.

  - **Be metal or Be composites** (non-critical purposes): composite materials, high-strength grades of Al, pyrolytic graphite, Si carbide, steel or Ti may substitute.

  - **Be oxide**: Al nitride or B nitride.

Be – environmental issues

- **Chronic beryllium disease (CBD)** or **berylliosis** has been known since the 1930s. Most reports were derived from the nuclear weapon industry and from the manufacture of fluorescent lamps containing Be-bearing phosphors. In order to contract CBD, an individual must be exposed to **airborne Be** in the form of a dust, mist or fume. Present exposure limit: **0.2 µg/m^3** 8 hours TWA.

- There has been considerable debate as to whether Be should be regarded as **carcinogenic to humans** → this is unlikely.

- Be intake from air and dust can be increased by 2 – 3 orders of magnitude in the vicinity of a point source, such as a **coal-fired power plant**. It is estimated that within the USA about 45% of airborne Be is due to **anthropogenic releases**.

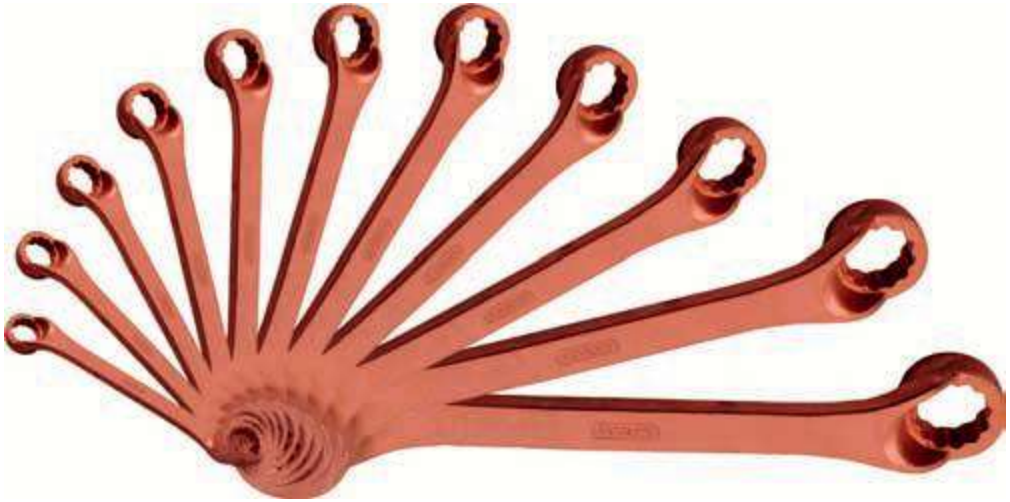
Be – outlook

- Since the early 1990s much of the world's Be raw material supply has been derived from a single source in **North America**. **China** has developed substantial production capacity for the production of Be hydroxide and Cu-Be hydroxide from imported beryl and domestic ores.

- **Cu-Be alloys** are widely used to provide an unmatched physical properties set to electronic and electrical components.

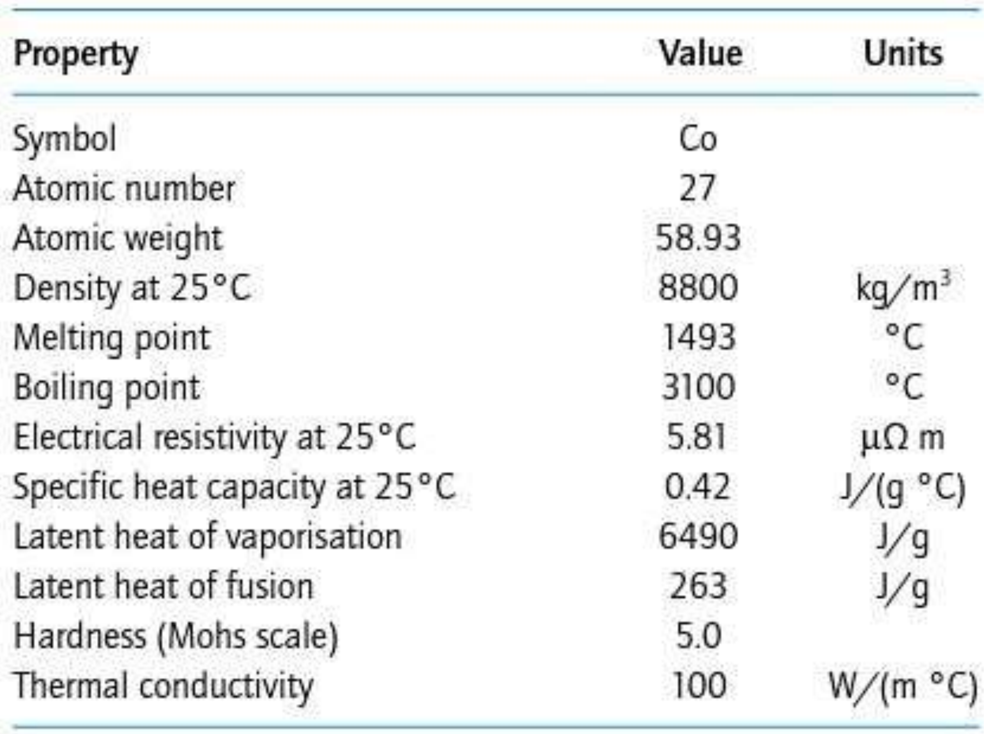
- The by mixing **U oxide with Be oxide** increases fuel rod utilization efficiencies.

- **Russia, Kazakhstan** and **China** will respond to future market demands.



Cobalt

Co – definitions and characteristics



Property	Value	Units
Symbol	Co	
Atomic number	27	
Atomic weight	58.93	
Density at 25°C	8800	kg/m^3
Melting point	1493	°C
Boiling point	3100	°C
Electrical resistivity at 25°C	5.81	μΩ m
Specific heat capacity at 25°C	0.42	J/(g °C)
Latent heat of vaporisation	6490	J/g
Latent heat of fusion	263	J/g
Hardness (Mohs scale)	5.0	
Thermal conductivity	100	W/(m °C)

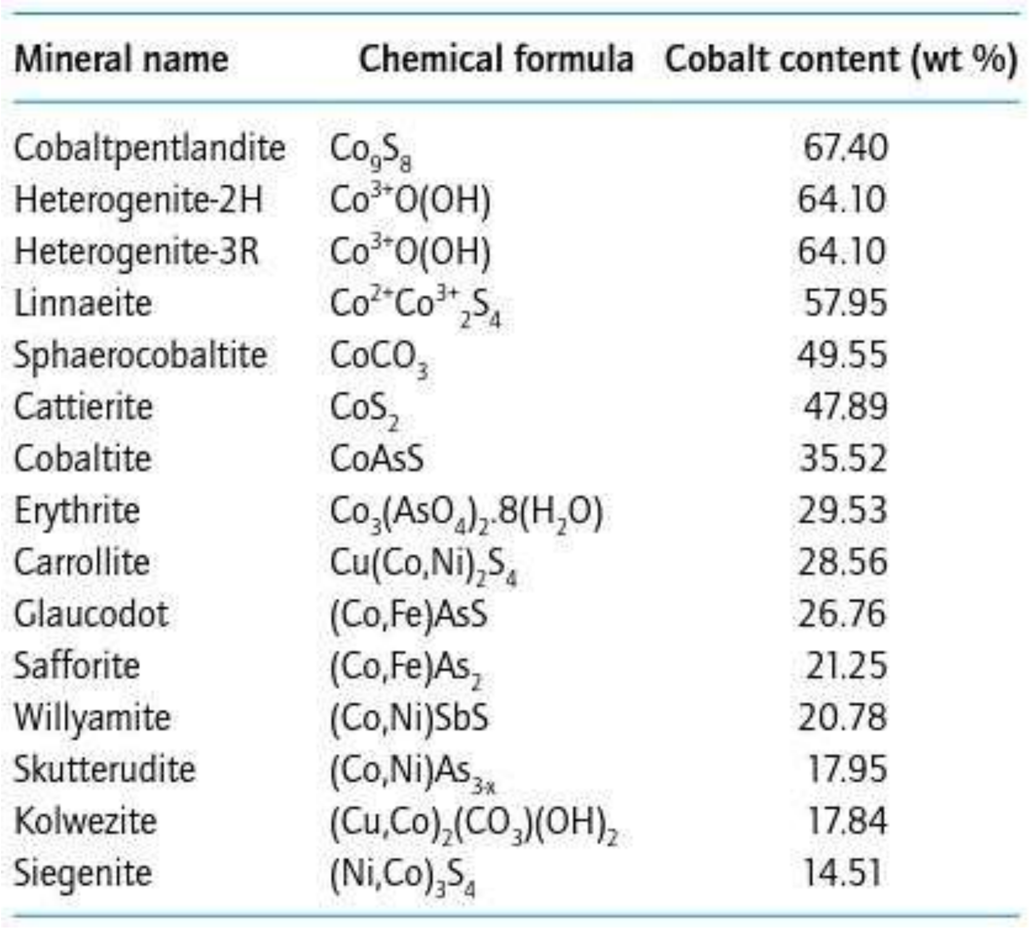
Co has been utilized since the **Bronze Age**, mainly to impart a rich **blue color** to glass, glazes and ceramics.

It was isolated as a pure metal in **1735**.

The demand for Co increased after the Second World War (jet engines and gas turbines).

Co demand has further accelerated in the past 30 years, reflecting the increased use of Co as an essential constituent of materials used in high-technology industries including **rechargeable batteries, superalloys and catalysts**.

Co – abundance in the Earth and mineralogy



Mineral name	Chemical formula	Cobalt content (wt %)
Cobaltpentlandite	Co_9S_8	67.40
Heterogenite-2H	$Co^{3+}O(OH)$	64.10
Heterogenite-3R	$Co^{3+}O(OH)$	64.10
Linnaeite	$Co^{2+}Co^{3+}{}_2S_4$	57.95
Sphaerocobaltite	$CoCO_3$	49.55
Cattierite	CoS_2	47.89
Cobaltite	$CoAsS$	35.52
Erythrite	$Co_3(AsO_4)_2.8(H_2O)$	29.53
Carrollite	$Cu(Co,Ni)_2S_4$	28.56
Glaucodot	$(Co,Fe)AsS$	26.76
Safforite	$(Co,Fe)As_2$	21.25
Willyamite	$(Co,Ni)SbS$	20.78
Skutterudite	$(Co,Ni)As_{3-x}$	17.95
Kolwezite	$(Cu,Co)_2(CO_3)(OH)_2$	17.84
Siegenite	$(Ni,Co)_3S_4$	14.51

- Co is a *d-block* **transition metal**, silver in colour.

- Co has 2 main oxidation states (**2^+** and **3^+**), and one naturally occurring isotope (**^{59}Co**).

- Co shows **siderophile** and **chalcophile** tendencies, has a **high melting point** (1493 °C) and is **ferromagnetic**.

- **Clarke: 15 – 30 ppm**. Co is most abundant in **ultramafic rocks** (110 ppm). Seawater: < 10 ppt.

- It preferentially bonds with Fe, Ni, Cu and S rather than with O, in a number of **sulfide** and **sulfarsenide** phases.

Co – major deposit classes

- The majority of Co production is achieved through recovery as a **by-product of Cu and Ni mining** in 4 principal geological settings:

1. **Hydrothermal**
2. **Magmatic**
3. **Lateritic**
4. **Fe-Mn nodules** (unexploited)

- **Hydrothermal deposits**: derived from fluids which have interacted with a variety of **mafic and/or ultramafic basement** rocks or are substantially derived from within **sedimentary basins** (e.g. Morocco, Idaho, Katangan Copperbelt).

- **IOCG deposits** (magmatic – hydrothermal)

- **Magmatic deposits**: concentrations of **Ni** and **Cu** with recoverable by-product Co (0.04 – 0.08 % Co) from **mafic – ultramafic magmas** (Kambalda, Sudbury).

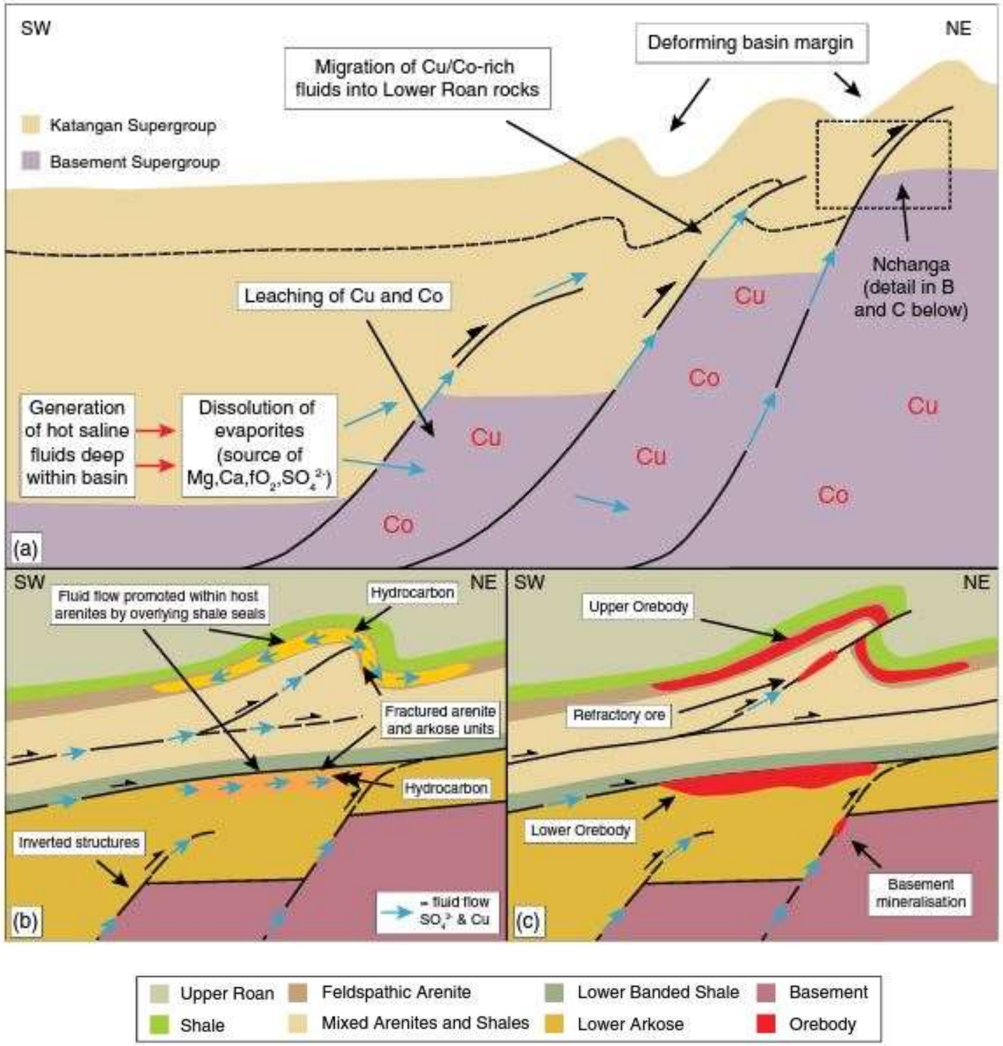


Figure 6.4 Schematic diagrams illustrating the development of the copper-cobalt deposit at Nchanga, Zambia. (a) Shows basinal brines migrating up reactivated faults at the margins of the Zambian Basin; (b) Shows migration of brines into gas-filled hydrocarbon traps, with overlying shales acting as seals; (c) Shows final distribution of orebodies at Nchanga. (Cu, copper; Co, cobalt; Mg, magnesium; Ca, calcium; SO_4^{2-}, sulfate; fO_2, oxygen fugacity.) (After McGowan et al., 2006.)

Co – bearing Ni laterite profiles

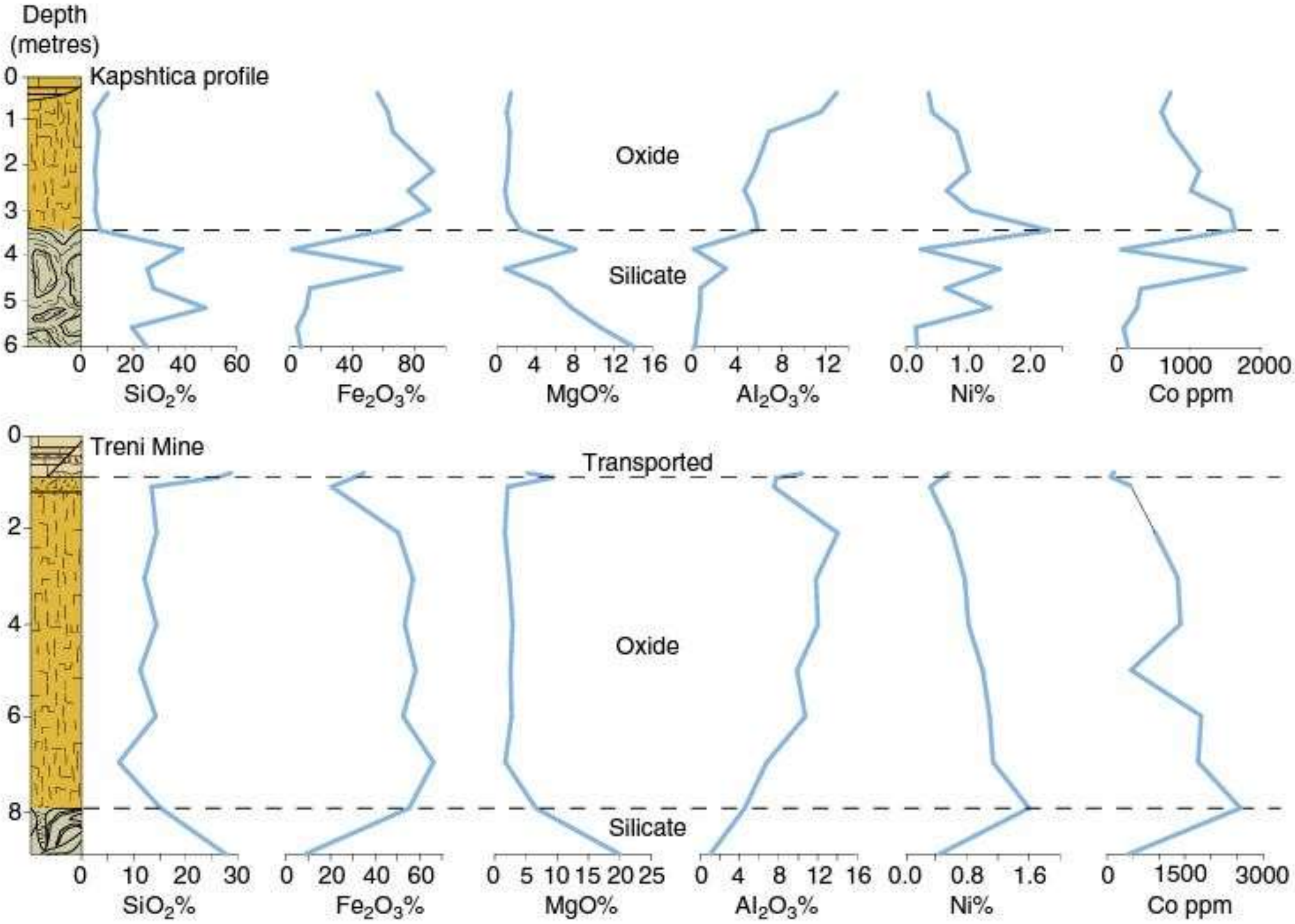
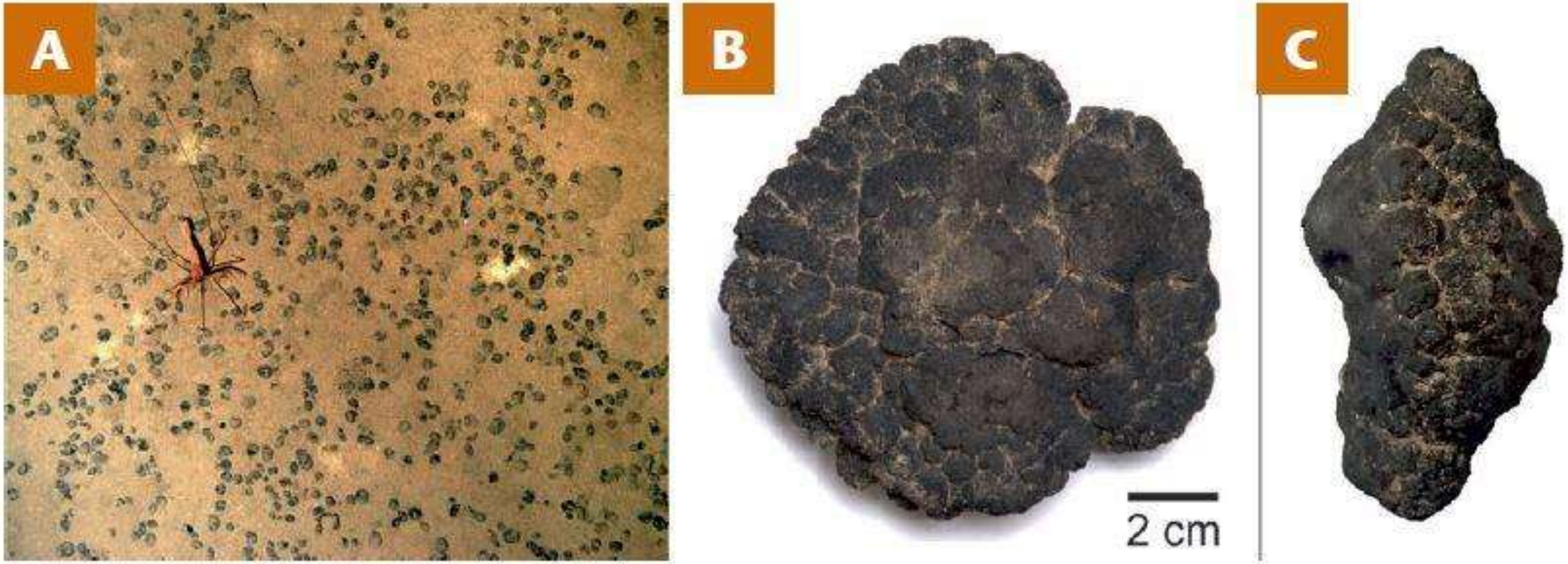


Figure 6.5 Geochemistry of a cobalt-bearing nickel laterite profiles. The profiles show the significant loss of SiO_2 and MgO at the silicate/oxide boundary and concomitant increases in Ni and Co. The profiles also indicate that the highest concentrations of Ni and Co within the profiles occur in close proximity to the silicate/oxide boundary. (SiO_2, silica; Fe_2O_3, iron oxide; MgO, magnesium oxide; Al_2O_3, aluminium oxide; Ni, nickel; Co, cobalt.) (After Thorne et al., 2012a.)

Ni-Co laterite deposits contain about **70% of world Ni resources** , but they also contain appreciable concentrations of Co (**0.025 – 0.18% Co**). The deposits are the product of pervasive weathering of **ultramafic rocks**, which initially contain between **0.06 and 0.09% Co**. Ni-Co laterite deposits can be grouped in 3 main categories:

1. **Hydrous silicate deposits**
2. **Clay silicate deposits**
3. **Oxide deposits**

Mn nodules and Co-rich ferromanganese crusts on the seafloor



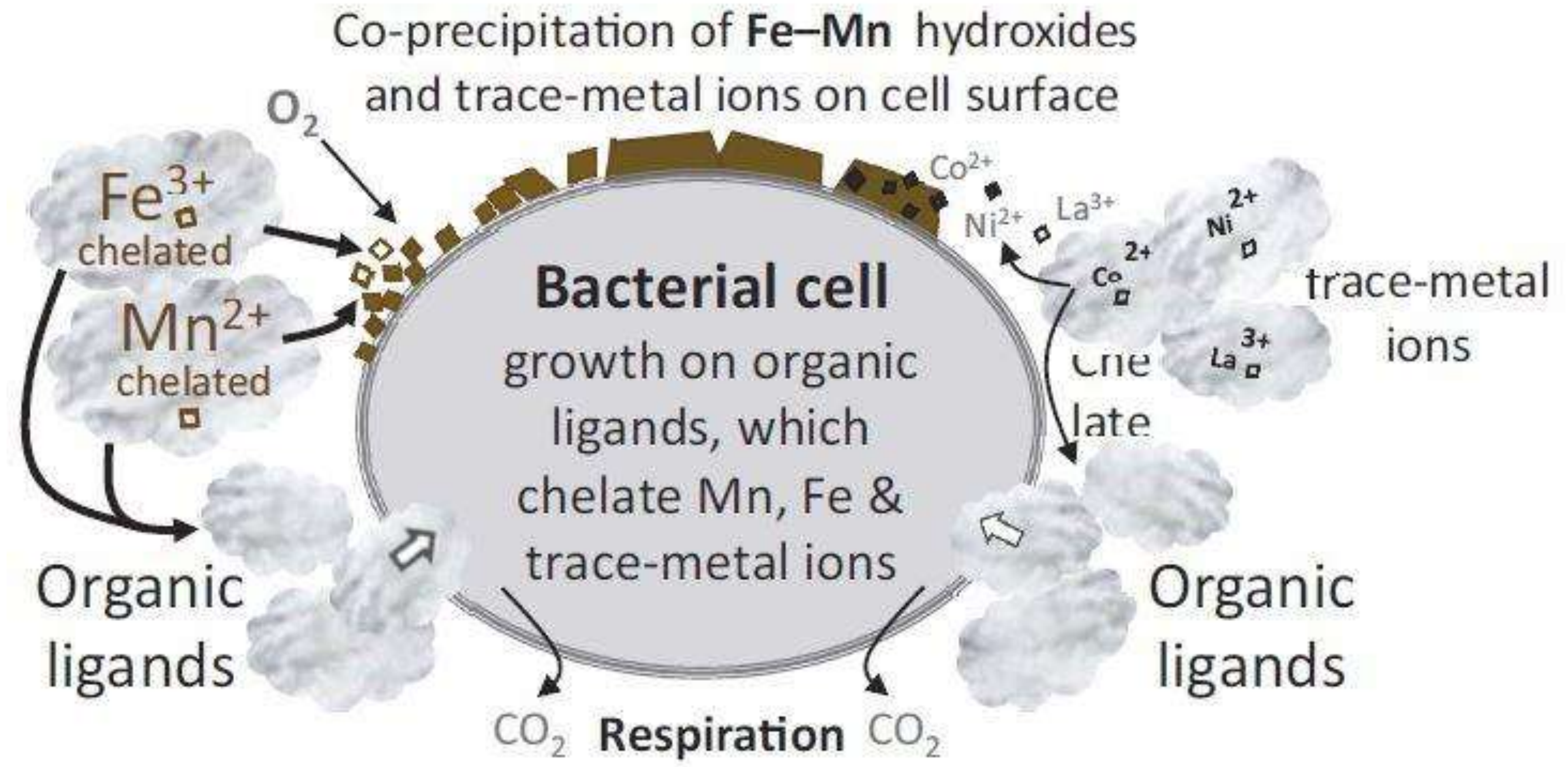
Ferromanganese nodules from the Clarion–Clipperton Zone (CCZ) in the Pacific Ocean. (**A**) Nodules on the sediment-covered abysall plain in the northeastern ‘Area of Particular Environmental Interest’ encountered on the RRS *James Cook* cruise JC120 using the autonomous underwater vehicle *Autosub6000*. (**B**) Upper surface of a large, 11 cm wide nodule. The rough botryoidal surface results from hydrogenetic growth. (**C**) Side view of the same nodule, showing the flattened shape and smoother base produced by diagenetic growth. Copyright British Geological Survey, National Oceanography Centre ©UKRI 2018.

Mn nodules and Co-rich ferromanganese crusts on the seafloor

Sample 35D193	Layers	Thickness (mm)	Mineralogy	Element concentration (%)					
				Mn	Fe	Ni	Cu	Co	P_2O_5
	III	0–20	Fe-vernadite, Mn-ferroxyhyte, quartz, buserite, goethite, haematite, feldspars	20.0	18.9	0.33	0.10	0.57	1.4
	II	20–50	Fe-vernadite, Mn-ferroxyhyte, goethite, clayey materials, feldspars, apatite, quartz, calcite, haematite	16.9	16.2	0.38	0.18	0.38	2.0
	1-2	50–65	Fe-vernadite, Mn-ferroxyhyte, apatite	16.8	13.3	0.31	0.17	0.30	9.3
	1-1	65–105	Fe-vernadite, Mn-ferroxyhyte, goethite, apatite, asbolane, calcite, quartz, feldspar	14.6	11.9	0.33	0.09	0.25	8.2
	R	105–165	Asbolane, vernadite, todorokite, ferrihydrite, apatite, calcite, quartz	8.9	5.8	0.47	0.11	0.13	14.0

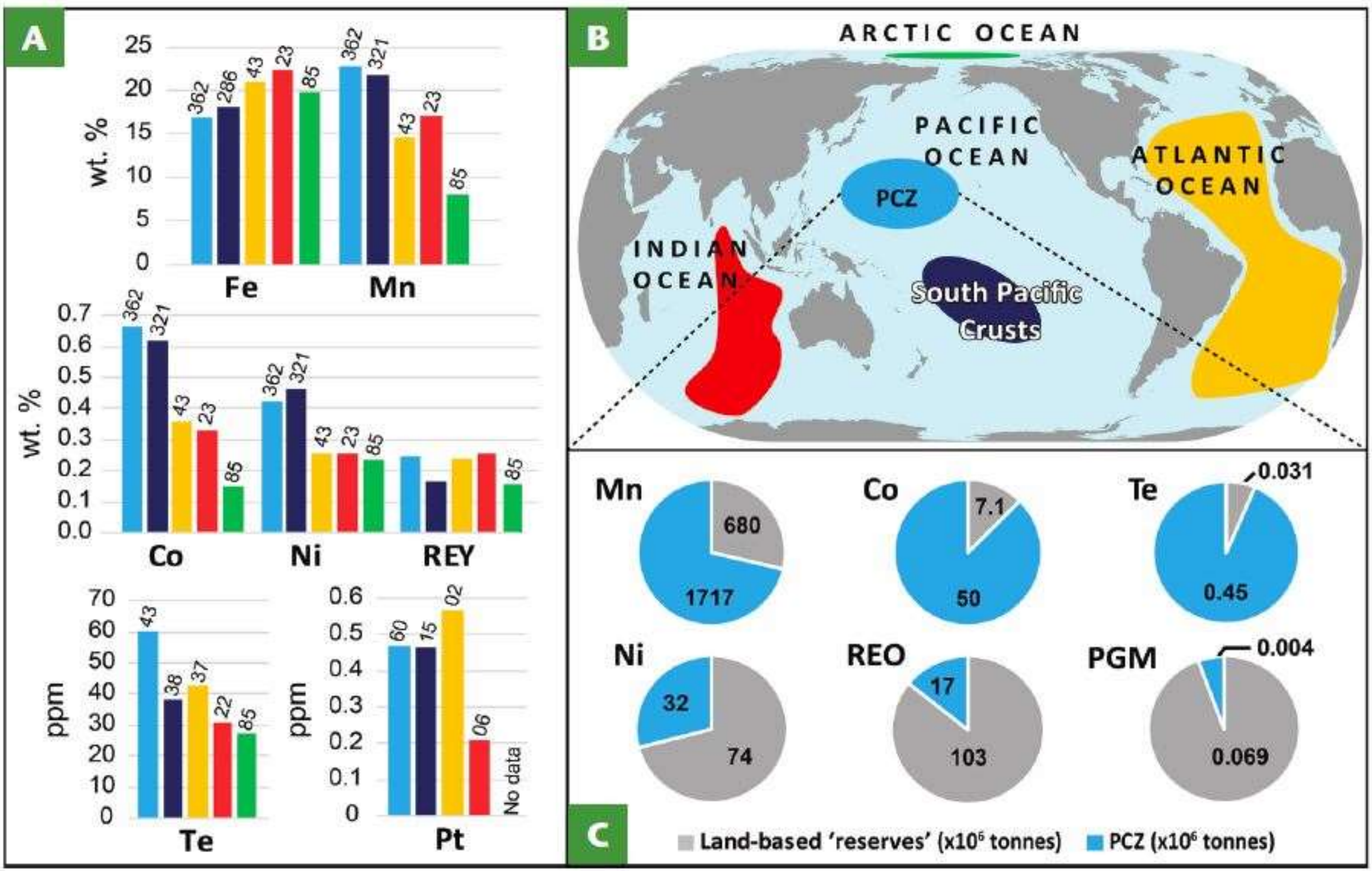
Figure 6.6 Thin section through a ferromanganese crust showing the mineralogical and geochemical variations within the sample. (Mn, manganese; Fe, iron; Ni, nickel; Cu, copper; Co, cobalt; P_2O_5, phosphorus pentoxide.) (After Glasby et al., 2007.)

Mn nodules and Co-rich ferromanganese crusts on the seafloor

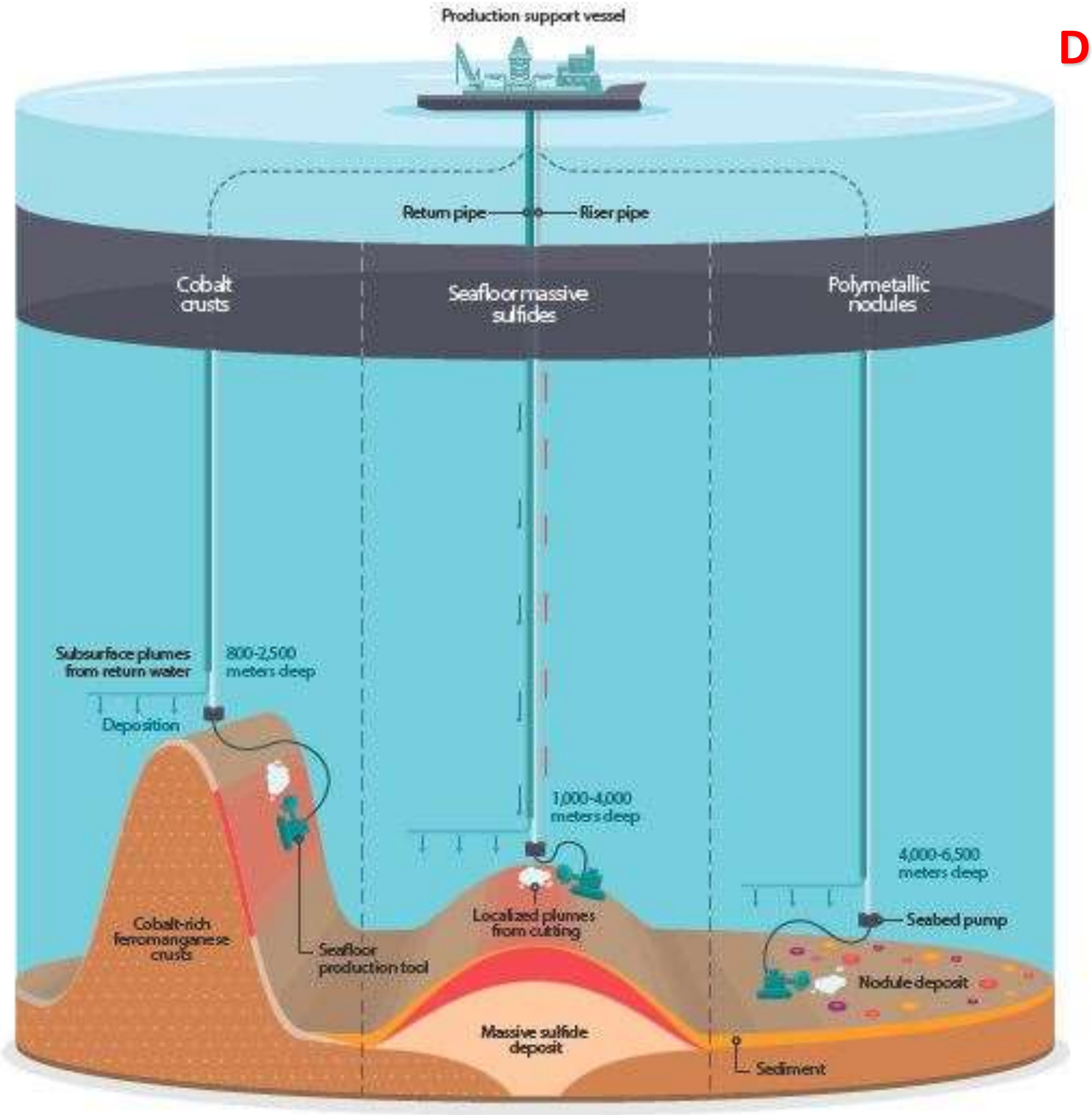


Schematic illustration of the microbial ligand consumption hypothesis for the formation of Fe–Mn encrustations. DIAGRAM: NINA KAMENNAYA

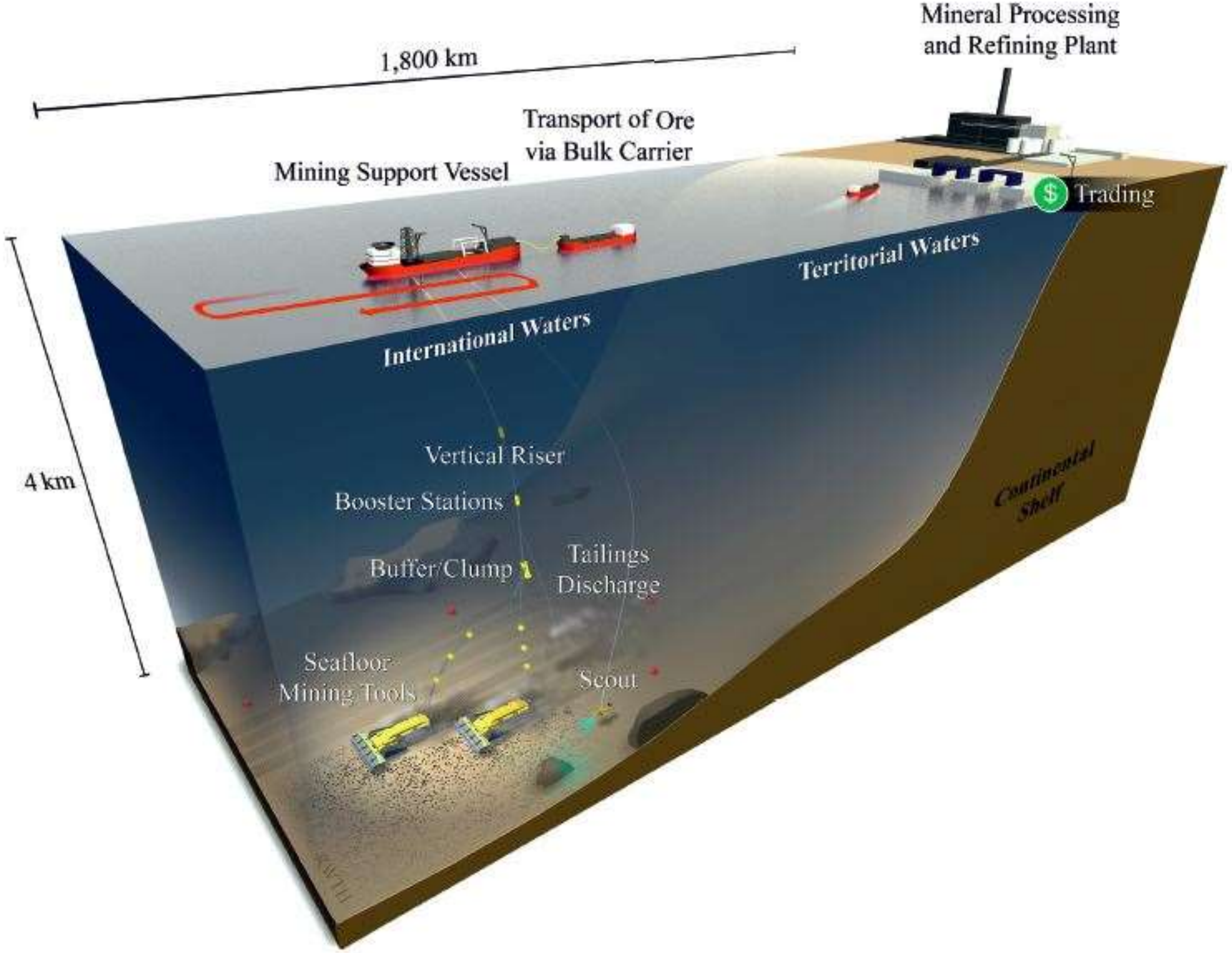
Metal grade, global resource distribution and estimated tonnages



Deep sea mining



Deep sea mining of Mn-Co nodules



Deep sea mining - impact

Environmental Impacts of Seabed Mining

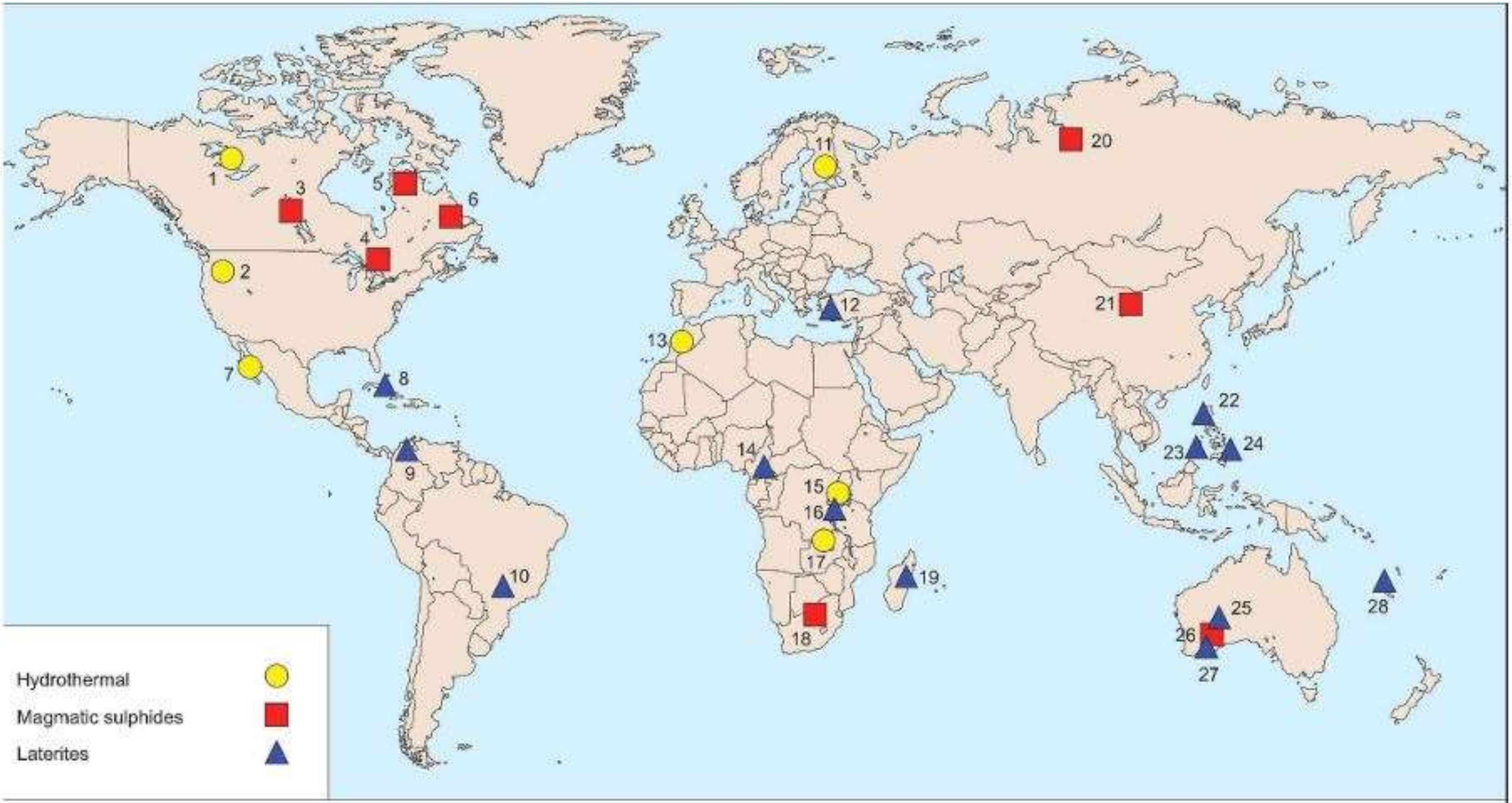
- permanent removal of hard substrate required by certain organisms/faunal communities
- effects of sediments, wastes, and other effluents (at bottom, mid-water and surface)
- noise
- vibration
- light
- leaks, spills, the effects of infrastructure corrosion
- operational discharges from the surface vessels*
- slow and different biological regeneration (especially of sessile communities)
- uncertain remediation potential
- vessel traffic for ore transport to shore* for land-based processing
- vessel-source air pollution*
- surface and mid-water marine community disturbance, especially if mining vessels remain on location for many months

Deep sea mining - advantages

Environmental Advantages of Seabed Mining (Contrasted with Terrestrial Mining)

- little or no overburden to remove (e.g. overlying rock, soil, vegetation cover)
- ore grades can be significantly higher than on land, meaning that less ore is required to provide the same amount of metal
- multiple metals can be obtained from a single site due to polymetallic nature of deposits
- no local human populations to be disrupted
- no permanent infrastructure

Co – major mines and districts



1 NICO
2 Idaho Cobalt Belt
3 Thompson
4 Sudbury
5 Raglan
6 Voisey's Bay
7 Boleo
8 Punta Gorda
9 Cerro Matoso
10 Barro Alto
11 Talvivaara
12 Çaldag
13 Bou Azer
14 Nkamouna
15 Kasese
16 Musongati
17 Central African Copperbelt
18 Bushveld
19 Ambatovy
20 Norilsk
21 Jinchuan
22 Acoje
23 Coral Bay
24 Taganito
25 Murrin Murrin
26 Kambalda
27 Ravensthorpe
28 New Caledonia

Figure 6.2 Major cobalt-producing mines and districts. The majority of new production is anticipated to be from laterite deposits.

Co – production by flash smelting of Ni sulfide ore and high-pressure acid leaching of laterite ore

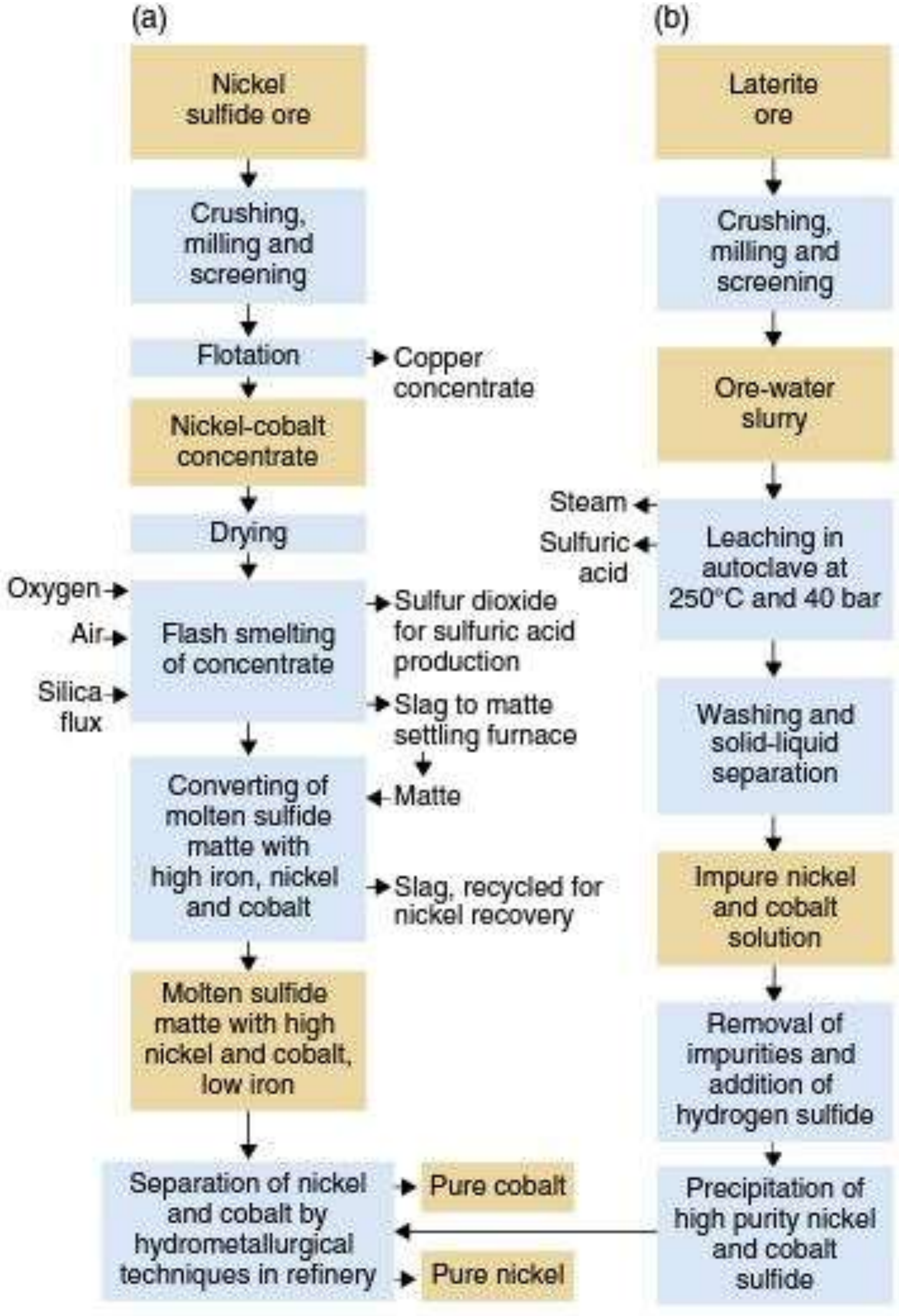
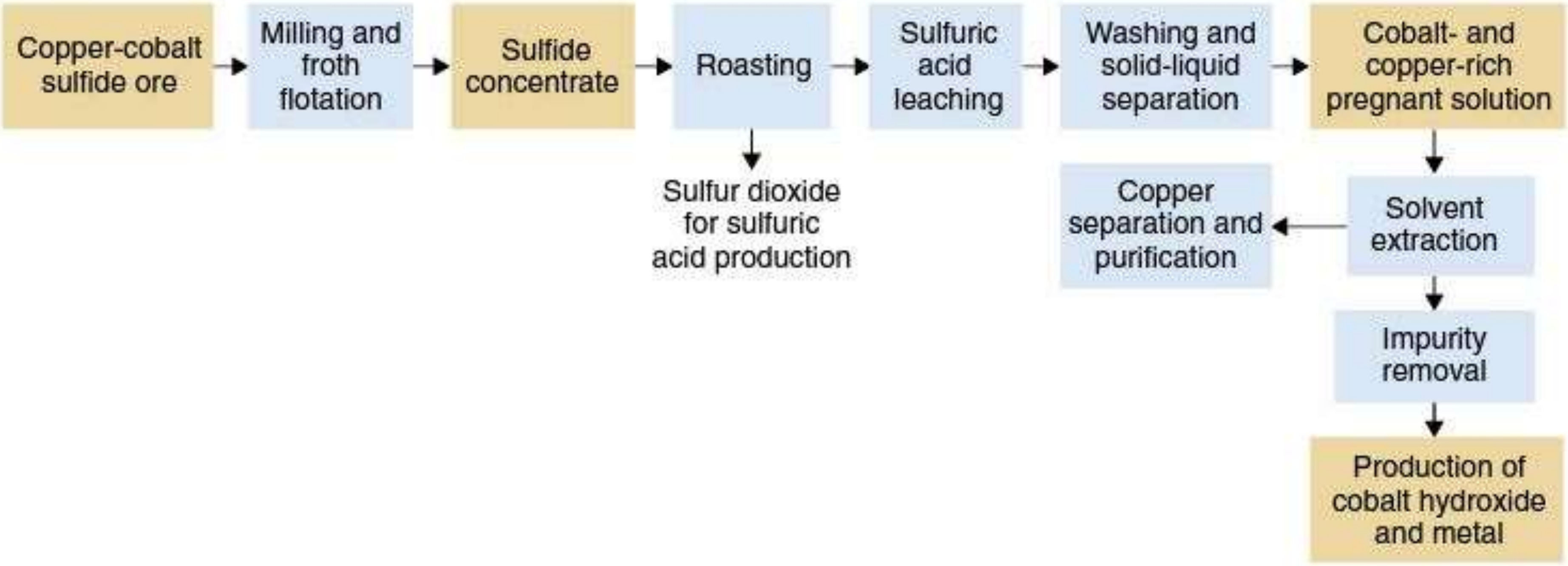


Figure 6.7 Generic flowsheet for the production of cobalt by (a) flash smelting and converting of nickel sulfide ore; and (b) high-pressure acid leaching of laterite ore.

Co – extraction from Cu-Co sulfide ores



Copper-cobalt sulfide ore

Milling and froth flotation

Sulfide concentrate

Roasting

Sulfur dioxide for sulfuric acid production

Sulfuric acid leaching

Washing and solid-liquid separation

Cobalt- and copper-rich pregnant solution

Solvent extraction

Copper separation and purification

Impurity removal

Production of cobalt hydroxide and metal

Figure 6.8 Schematic flowsheet for the extraction of cobalt from copper–cobalt sulfide ores.

Co – extraction from weathered Cu-Co ore using whole ore leach (WOL)

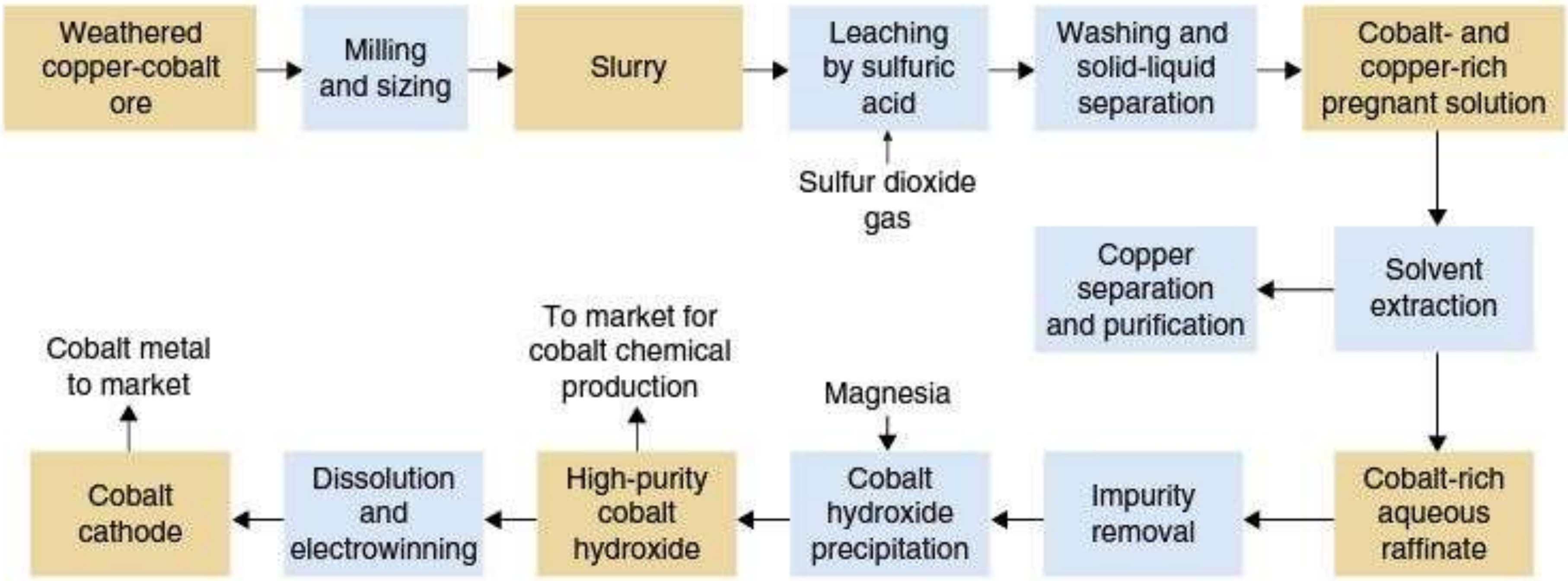


Figure 6.9 Schematic flowsheet for the extraction of cobalt from weathered copper–cobalt ore using whole ore leach (WOL).

Co – specifications and uses

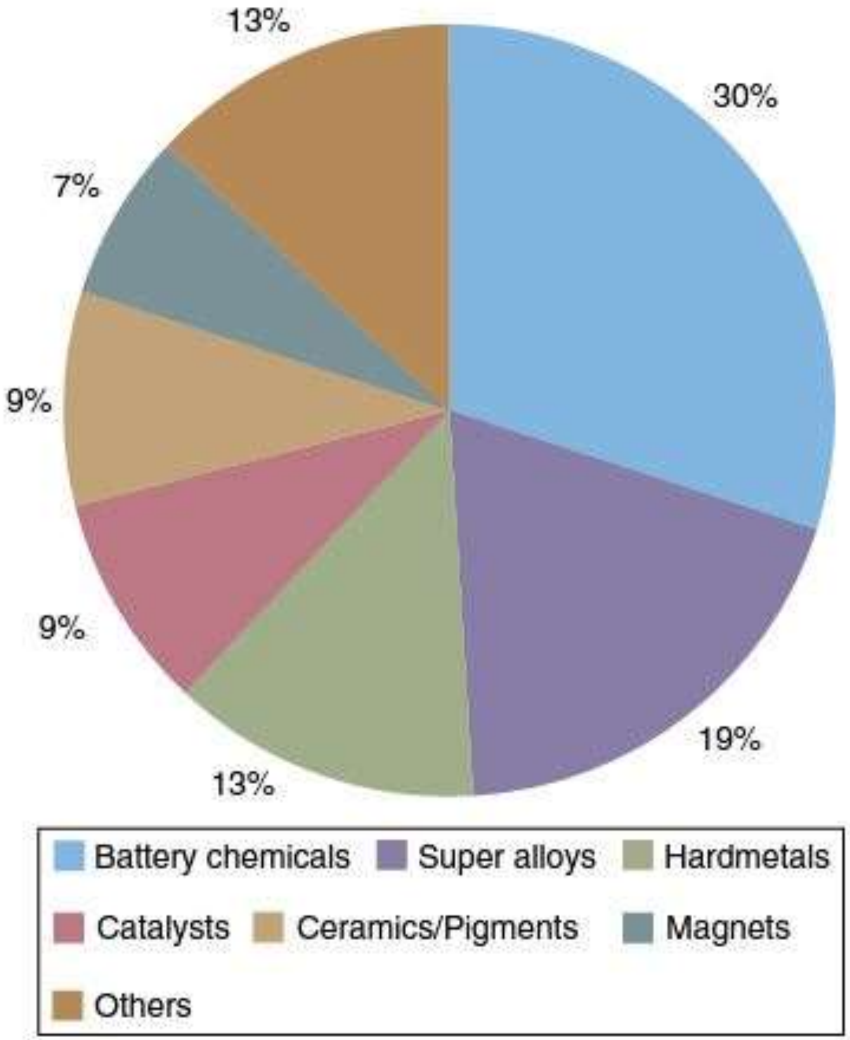


Figure 6.16 Estimated cobalt demand by end-use in 2011. (Data from Cobalt Development Institute, 2012a.)

- Co continues to have few applications in its pure form and is most commonly used as an **alloy constituent** or **chemical compound**, where its chemical and wear resistance, magnetic properties and high T strength are used.

- **Batteries**: **Li-ion** (up to 60% Co as Li-Co oxide); **NiMh** (hybrid electric vehicles); Co oxide in **Ni-Cd** batteries.

- **Superalloys and magnet alloys**: jet engines and turbines, **Sm-Co** and Al-Ni-Co magnets.

- **Catalysts**: catalytic processes account for 10% of all Co consumption. Polymerization of plastic resins, GTL (gas-to-liquid, Shell®).

- Binder material in **hard materials**, **diamond tool** applications, HSS, **pigments**, **cancer treatment**.

Co – recycling and substitution

- Recycling
  - Price volatility, geopolitics of supply and potential cost and environmental benefits drive the recycling of Co.

  - **Scrap metal, spent catalysts** and **rechargeable batteries** are the most readily amenable Co-bearing products for recycling.

  - It is not possible to recycle Co from **pigments**, **glass** and **paint**.

  - Recycling of alloy and hard metal scrap is generally operated by and within the **superalloy and metal carbide sector**.

- Substitution
  - **Magnets**: Ba or Sr ferrites, Nd-Fe-B or Ni-Fe alloys.

  - **Paints:** Ce, Fe, Pb, Mn or V.

  - **Jet engines and petroleum catalysts**: Ni and Ni-based alloys.

  - **Li-ion batteries**: Fe-P-Mn, Ni-Co-Al or Ni-Co-Mn alloys.

Co – global mine production

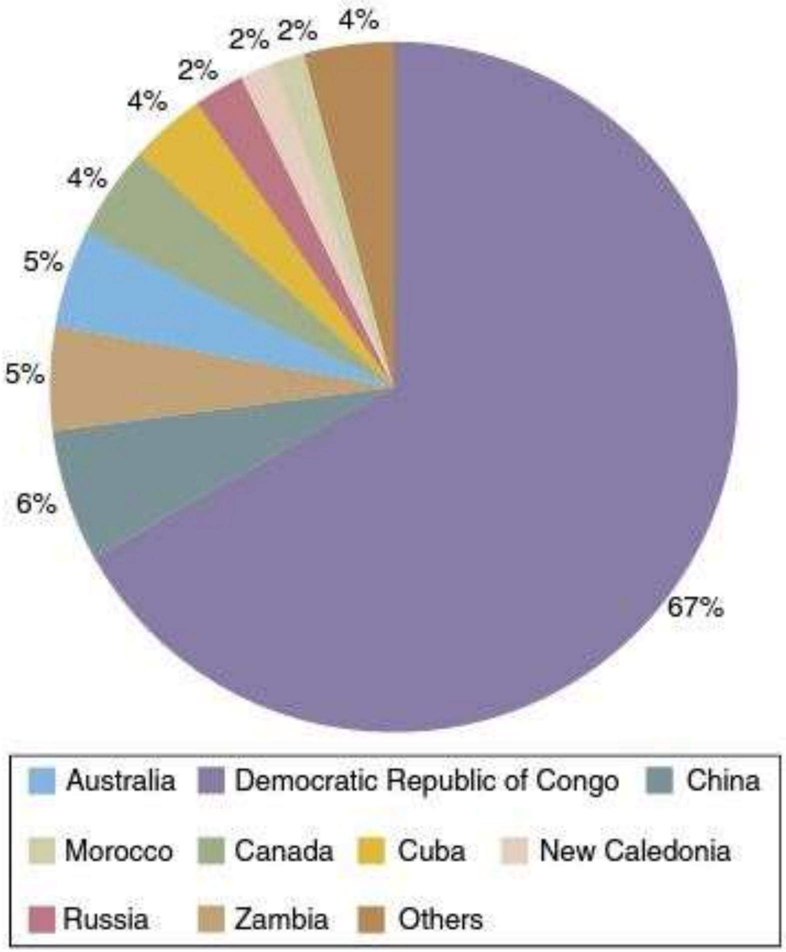


Figure 6.11 The distribution of global mine production of cobalt in 2010 by country. (Data from British Geological Survey, 2012.)

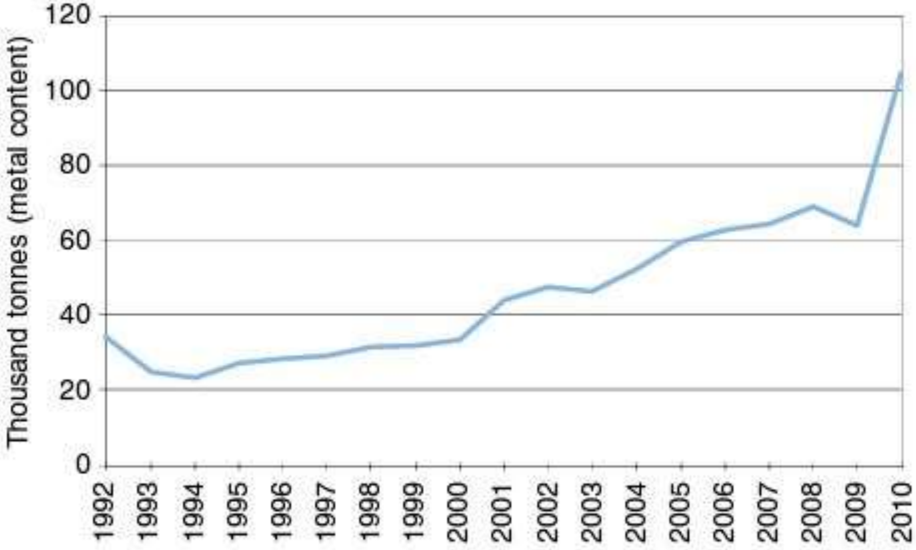


Figure 6.10 Global mine production of cobalt from 1992 to 2010. (Data from British Geological Survey World Mineral Statistics database.)

Co – environmental issues

- Co in the environment is derived from both **natural** and **anthropogenic sources** (mining and processing of Co-containing ores, agricultural application of Co-containing fertilizers, combustion of fossil fuels).

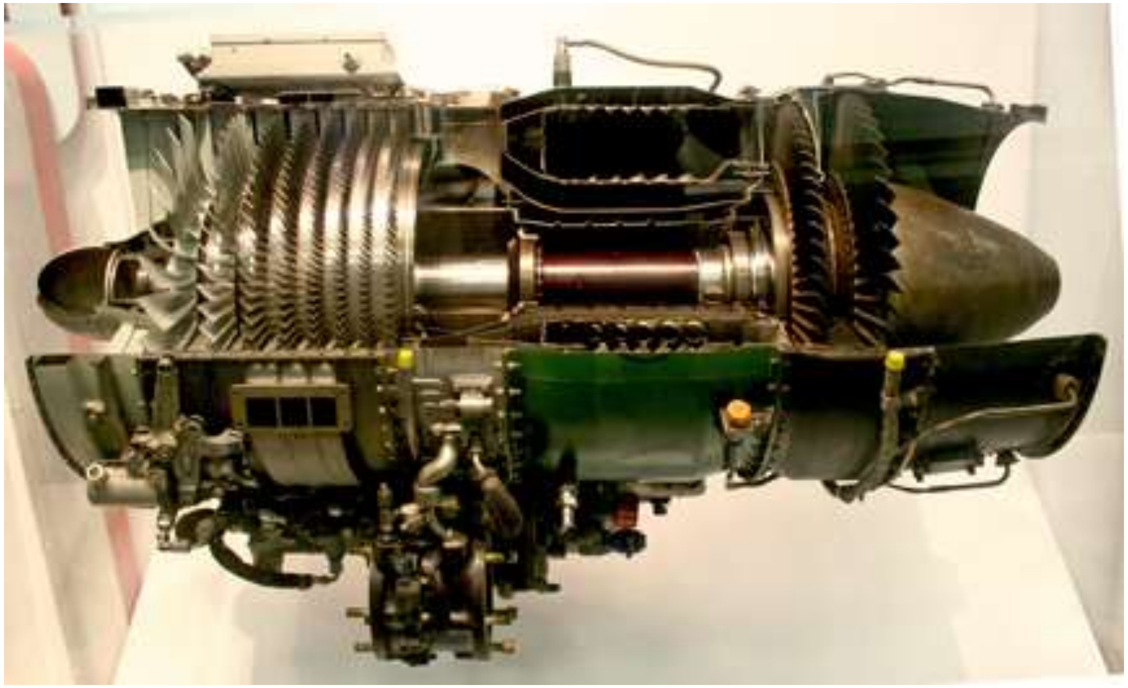
- The average concentration of Co in **soils** is **8 ppm**.

- Co is an essential component of **vitamin** $\mathbf{B_{12}}$, cobalamin. Co overexposure includes reduced food consumption, decreased body weight, blood disorders, debility.

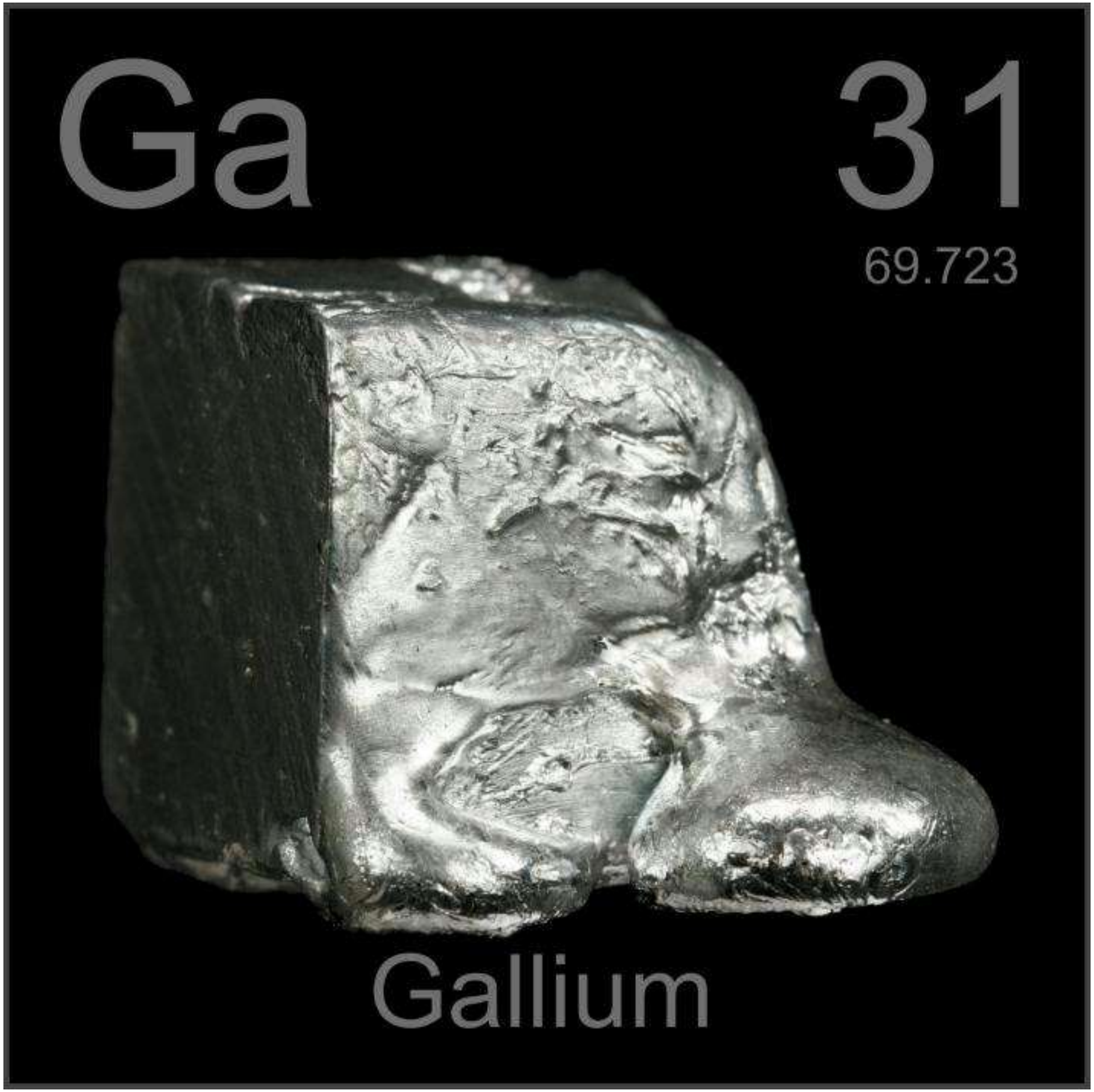
- Inhalation of high concentrations of Co is linked to **lung diseases** such as asthma and pneumonia (only workers exposed to high levels of Co).

Co – outlook

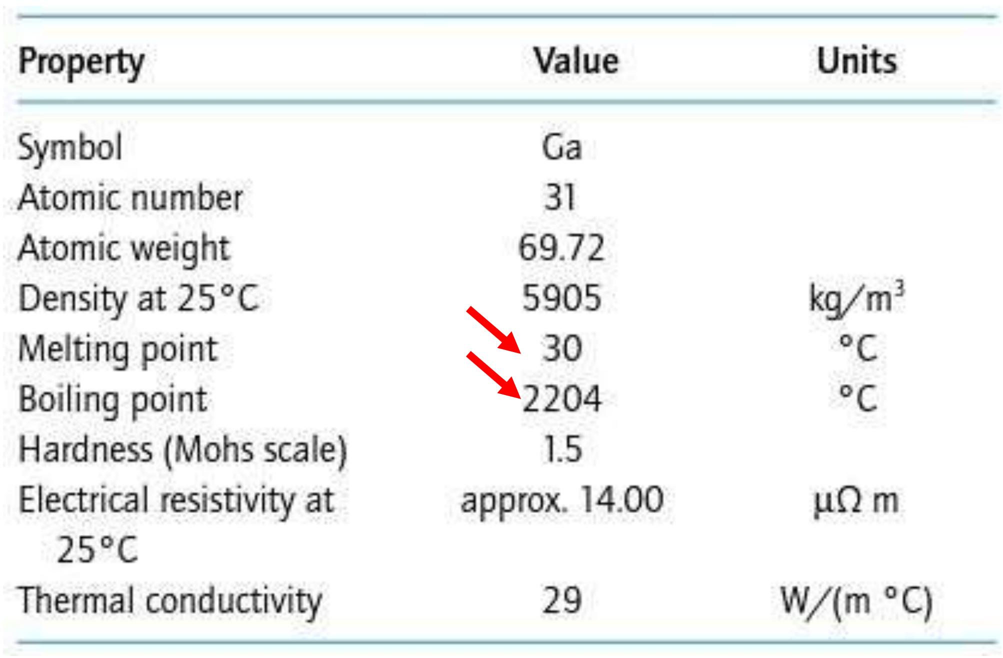
- There are many potential new sources of Co, both onshore, in Canada, Western Australia, the DRC, Zambia and Madagascar, and offshore in deep sea nodules.
- Since 2002 Co consumption in Asia has increased significantly (**rechargeable batteries** and **catalysts**).
- The use of Co in **superalloys** is expected to increase in response to continuing expansion of the global **aerospace market**.



Gallium



Ga – definitions and characteristics



Property	Value	Units
Symbol	Ga	
Atomic number	31	
Atomic weight	69.72	
Density at 25°C	5905	kg/m^3
Melting point	30	°C
Boiling point	2204	°C
Hardness (Mohs scale)	1.5	
Electrical resistivity at 25°C	approx. 14.00	μΩ m
Thermal conductivity	29	W/(m °C)

Ga was discovered in **1875** by Paul Émile Lecoq de Boisbaudran: he named the new element "*gallia*" after the Latin name for France.

As a pure metal, Ga is silvery-white. It is a relatively soft metal, with a **low melting point** but a comparatively **high boiling point**. Combined with a **low vapor pressure**, even at high temperatures, this gives **the longest liquid range of any metal**.

As a liquid it will **wet glass and skin**, and will readily **contaminate other metals** by diffusing into their lattice structure.

Ga – abundance in the Earth and mineralogy

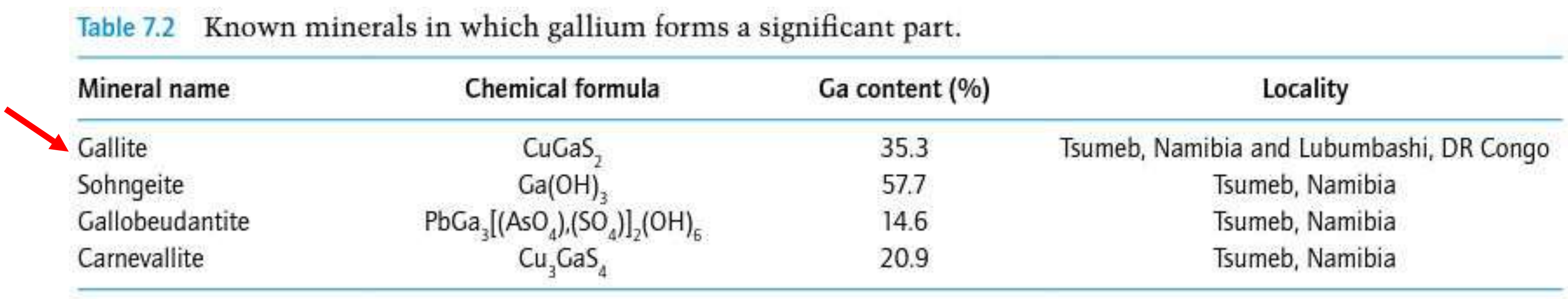


Table 7.2 Known minerals in which gallium forms a significant part.

Mineral name	Chemical formula	Ga content (%)	Locality
Gallite	$CuGaS_2$	35.3	Tsumeb, Namibia and Lubumbashi, DR Congo
Sohngeite	$Ga(OH)_3$	57.7	Tsumeb, Namibia
Gallobeudantite	$PbGa_3[(AsO_4),(SO_4)]_2(OH)_6$	14.6	Tsumeb, Namibia
Carnevallite	Cu_3GaS_4	20.9	Tsumeb, Namibia

- Ga is **magnetic** and a **good conductor** of both **electricity** and **heat**. It exhibits a noticeable **anisotropy** in **electrical resistivity** dependent upon the **orientation of crystals** within its structure.

- **Clarke: 19 ppm**. It does not occur in nature as a native metal, but instead it substitutes for other elements in certain minerals.

- The main Ga-bearing mineral is **gallite**. Currently there are no mines worked primarily for Ga, because it is recovered as a **by-product** of processing **bauxite** or **sphalerite**.

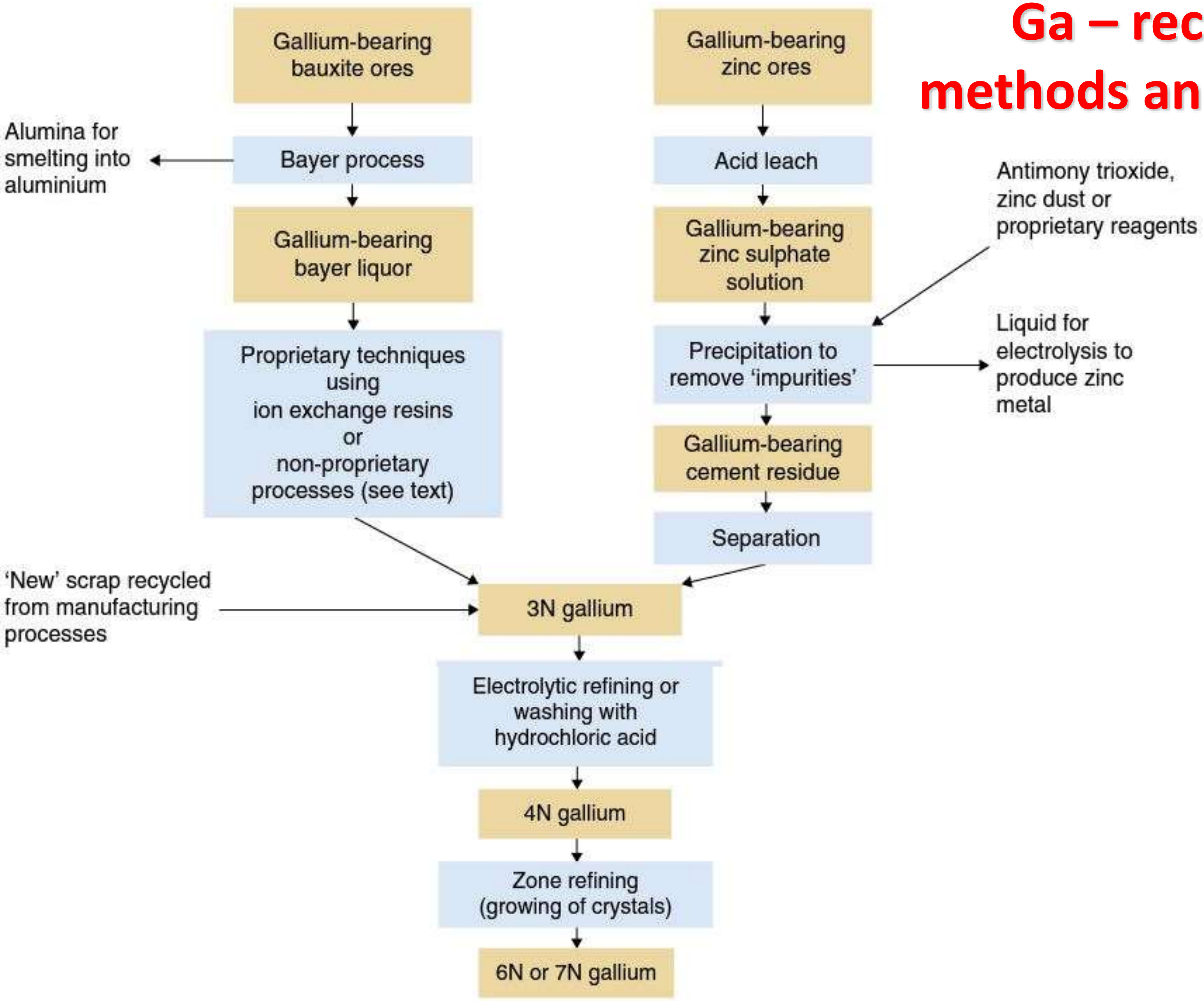
Sources of Ga

- **BAUXITE**: the ratio of Ga to Al, and therefore the concentration of Ga, in bauxite increases with **greater intensity of weathering**. Ga also appears to be more abundant where the bauxite was derived from **alkali source rocks**. The average Ga content in bauxite is ≈ **50 ppm**, although it can vary from 10 to 160 ppm.

- **SPHALERITE (ZnS)**: Ga concentrations in the zinc ore are known to **increase as the T of deposition decreases** (e.g. **MVT**), although it can still be present in intermediate and higher-T deposits. The composition of sphalerite from each metallogenic region is distinctive (e.g. no Ga in European MVT deposits).

- Ga also occurs in other **aluminosilicate minerals**, **geothermal fields** in volcanic zones, in association with **phosphate ores** and some **coal deposits**. Ga concentrations of 149 – 320 ppm have been reported in **fly ash** from the combustion of coal (not commercially viable).

Ga – recovery methods and refining



Gallium-bearing bauxite ores

Bayer process

Alumina for smelting into aluminium

Gallium-bearing bayer liquor

Proprietary techniques using ion exchange resins or non-proprietary processes (see text)

Gallium-bearing zinc ores

Acid leach

Gallium-bearing zinc sulphate solution

Antimony trioxide, zinc dust or proprietary reagents

Precipitation to remove 'impurities'

Liquid for electrolysis to produce zinc metal

Gallium-bearing cement residue

Separation

'New' scrap recycled from manufacturing processes

3N gallium

Electrolytic refining or washing with hydrochloric acid

4N gallium

Zone refining (growing of crystals)

6N or 7N gallium

Schematic diagram of the processes involved in extracting gallium.

Ga – specifications and uses

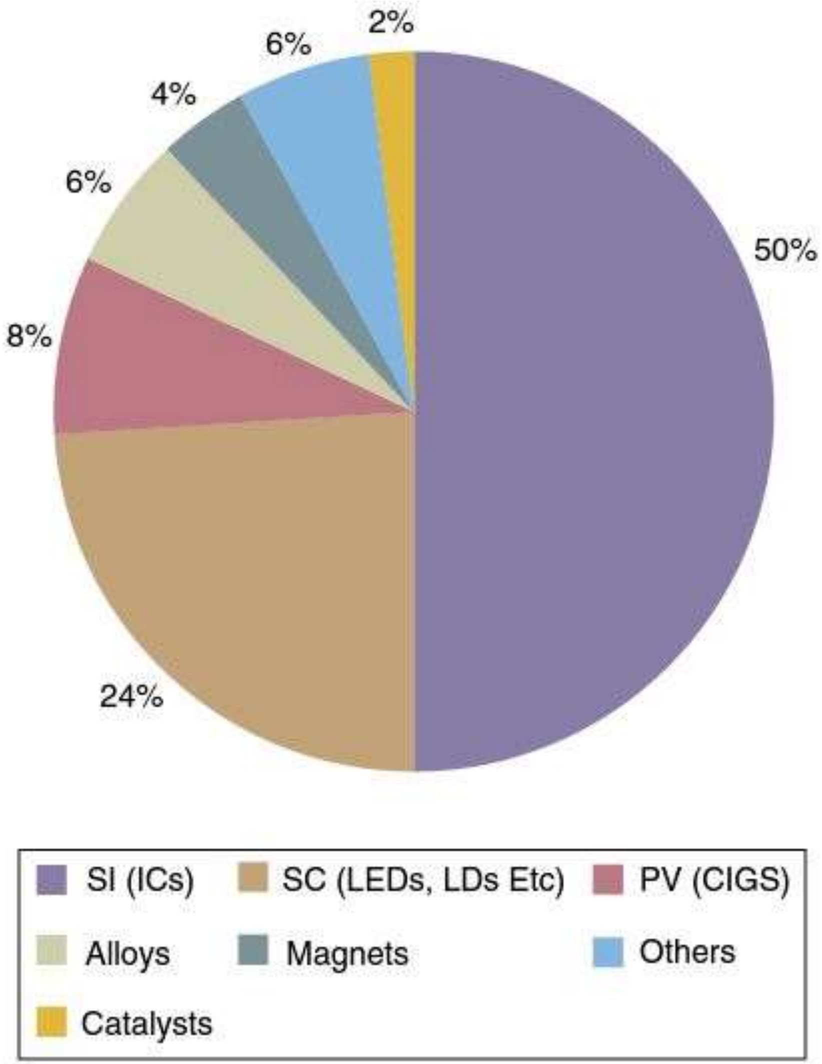


Figure 7.7 Estimated demand for gallium in 2010. Notes: SI, semi-insulating; SC, semiconducting; PV, photovoltaic.

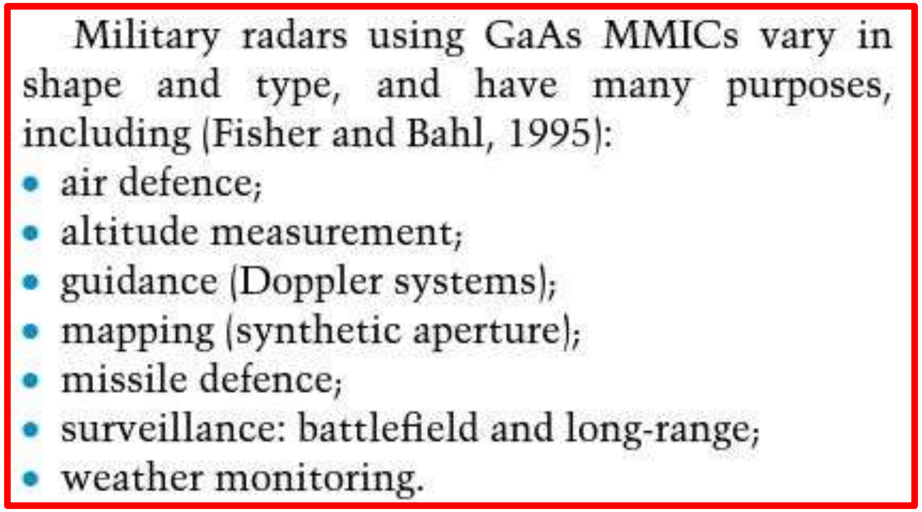
Ga is used in a number of different forms:

- **Ga metal**: eutectic alloys, magnets (Nd-Fe-B), molecular beam epitaxy, nuclear weapon pits (alloyed with plutonium), thermometers, thin-film deposition.

- **Ga antimonide**: infrared FLIR systems for night–time navigation, LEDs, missile homing guidance systems, thermal imaging, high-speed electronic circuits.

- **Ga arsenide**: compound semiconductors, cell phones, military applications, Infrared Emitting Diodes (IREDs), Laser Emitting Diodes (LEDs); wireless communications.

Ga – uses



Military radars using GaAs MMICs vary in shape and type, and have many purposes, including (Fisher and Bahl, 1995):

- air defence;
- altitude measurement;
- guidance (Doppler systems);
- mapping (synthetic aperture);
- missile defence;
- surveillance: battlefield and long-range;
- weather monitoring.

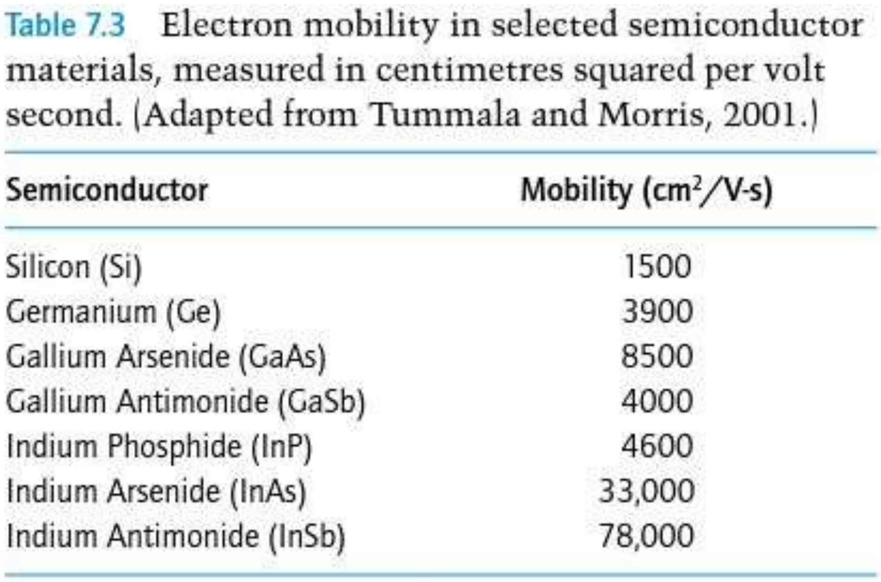


Table 7.3 Electron mobility in selected semiconductor materials, measured in centimetres squared per volt second. (Adapted from Tummala and Morris, 2001.)

Semiconductor	Mobility (cm^2/V-s)
Silicon (Si)	1500
Germanium (Ge)	3900
Gallium Arsenide (GaAs)	8500
Gallium Antimonide (GaSb)	4000
Indium Phosphide (InP)	4600
Indium Arsenide (InAs)	33,000
Indium Antimonide (InSb)	78,000

- **Ga chemicals**: Ga nitrate (pharmaceutical), Ga trichloride, Ga trioxide, triethyl-Ga, trimethyl-Ga.
- **Ga nitride**: laser diodes, LEDs.
- **Ga phosphide**: LEDs, photovoltaics, thin-film solar cells (TFSC).

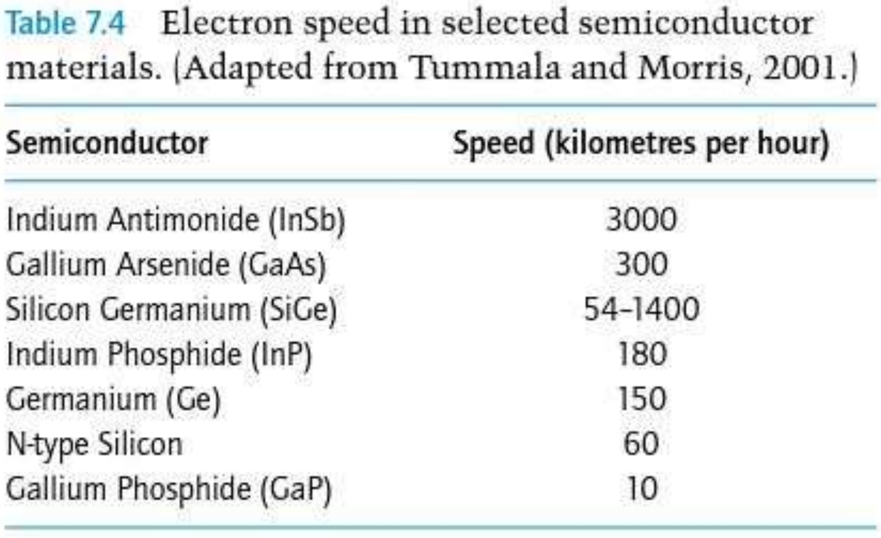


Table 7.4 Electron speed in selected semiconductor materials. (Adapted from Tummala and Morris, 2001.)

Semiconductor	Speed (kilometres per hour)
Indium Antimonide (InSb)	3000
Gallium Arsenide (GaAs)	300
Silicon Germanium (SiGe)	54-1400
Indium Phosphide (InP)	180
Germanium (Ge)	150
N-type Silicon	60
Gallium Phosphide (GaP)	10

Ga – GaN LEDs

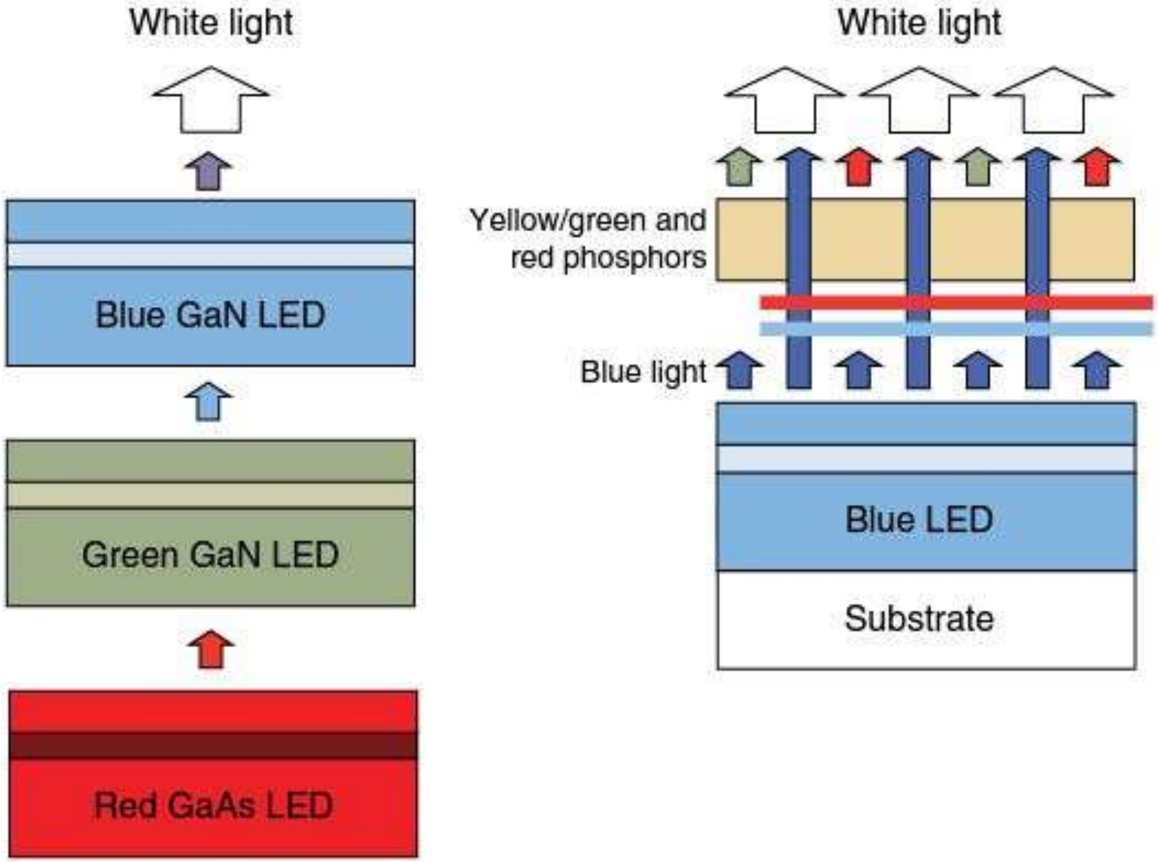
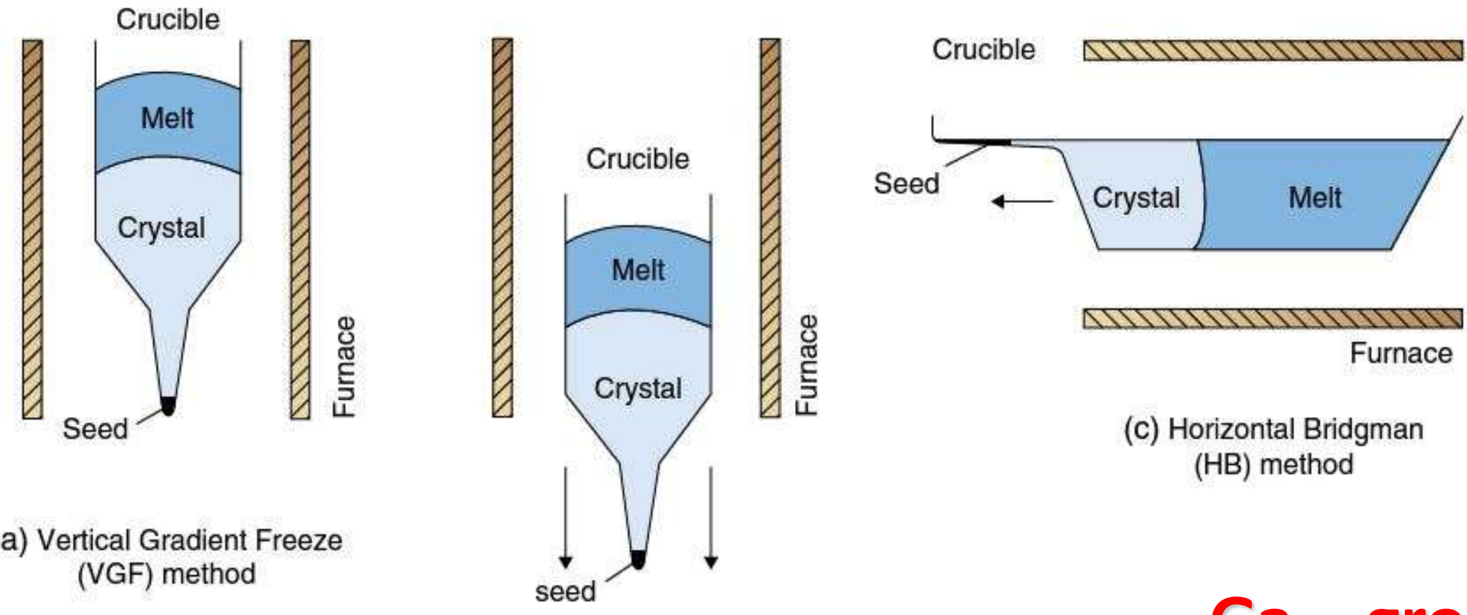


Figure 7.3 Two ways to produce white light from GaN LEDs (DenBaars, 2008).

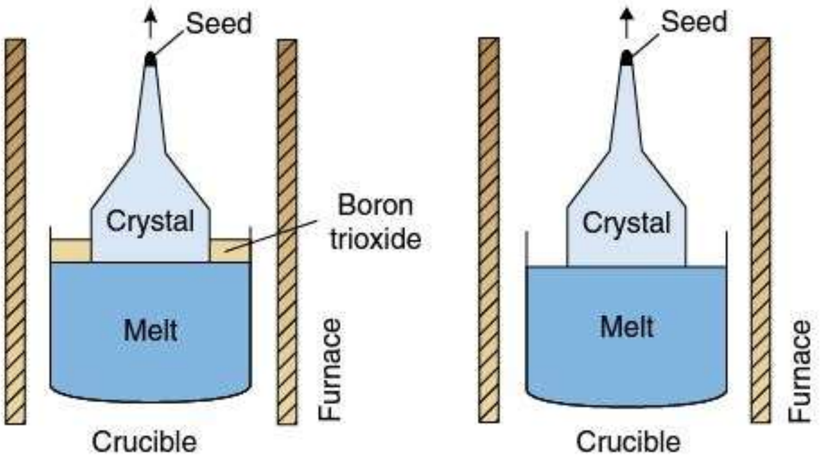
Ga – growing single crystals of GaAs substrate



(a) Vertical Gradient Freeze (VGF) method

(b) Vertical Bridgman (VB) method

(c) Horizontal Bridgman (HB) method



(d) Liquid Encapsulated Czochralski (LEC) method

(e) Czochralski (CZ) method

Figure 7.2 An illustration of most common manufacturing technologies for growing single crystals of GaAs substrate.

Ga – substitution

- Ga has some unique properties which make it difficult to substitute.
- **Si** can be used instead of GaAs in photovoltaic cells (reducing efficiency).
- **Ge** can be used as a substitute for GaAs in some electronics.
- **Organic-based liquid-crystal displays** can substitute for Ga in certain LED applications.
- **Indium phosphide** can be used for infrared laser diodes, and He-Ne lasers compete with GaAs in visible laser diode applications.
- **GaN** is the latest development in the field of semiconductors.

Ga – secondary recovery

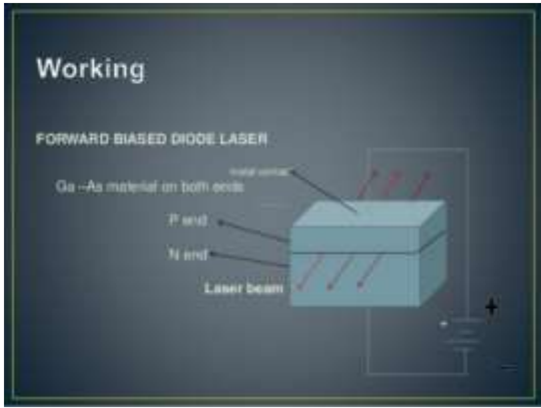
- Since one of the main uses of Ga is in **compound semiconductor wafers**, and their fabrication typically generates around 60% scrap, recovered Ga from this waste is an extremely important source of the metal. The wastes from the manufacture of Ga arsenide (**GaAs**) and Ga nitride (**GaN**) wafers, are the metal's **most important secondary source**.

From compound semiconductor manufacture, the main sources of gallium scrap include (Burke, 2011):

- boule ends and chunks;
- broken wafers – from all stages of fabrication;
- cutting and polishing sludges;
- defective devices;
- dust and residues in wastewater filters;
- epitaxial growth wastes;
- kerf generated during wafer slicing;
- liquids following etching;
- residues in GaAs single crystal reactors;
- substandard GaAs ingots.

The gallium content in such scrap can be between one per cent (for example, from wastewater filters) and 99.99 per cent (frozen metal) (Kramer, 2002), depending at which stage in the fabrication process the scrap is generated.

Typically the recovery and recycling of gallium is economically viable from throughout the production process of gallium-containing compound semiconductors.



Ga – virgin Ga production

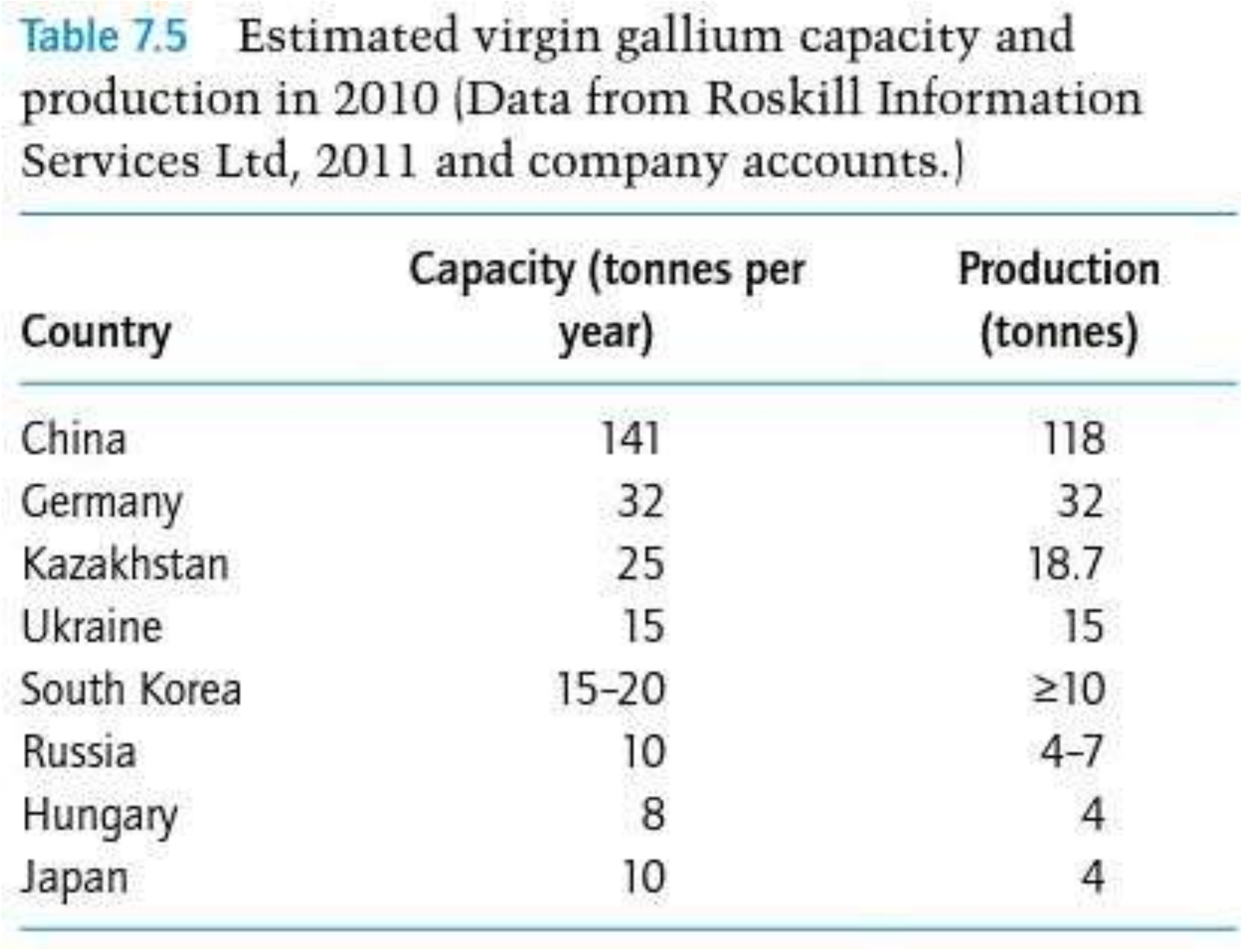


Table 7.5 Estimated virgin gallium capacity and production in 2010 (Data from Roskill Information Services Ltd, 2011 and company accounts.)

Country	Capacity (tonnes per year)	Production (tonnes)
China	141	118
Germany	32	32
Kazakhstan	25	18.7
Ukraine	15	15
South Korea	15-20	≥10
Russia	10	4-7
Hungary	8	4
Japan	10	4

Ga – secondary recovery

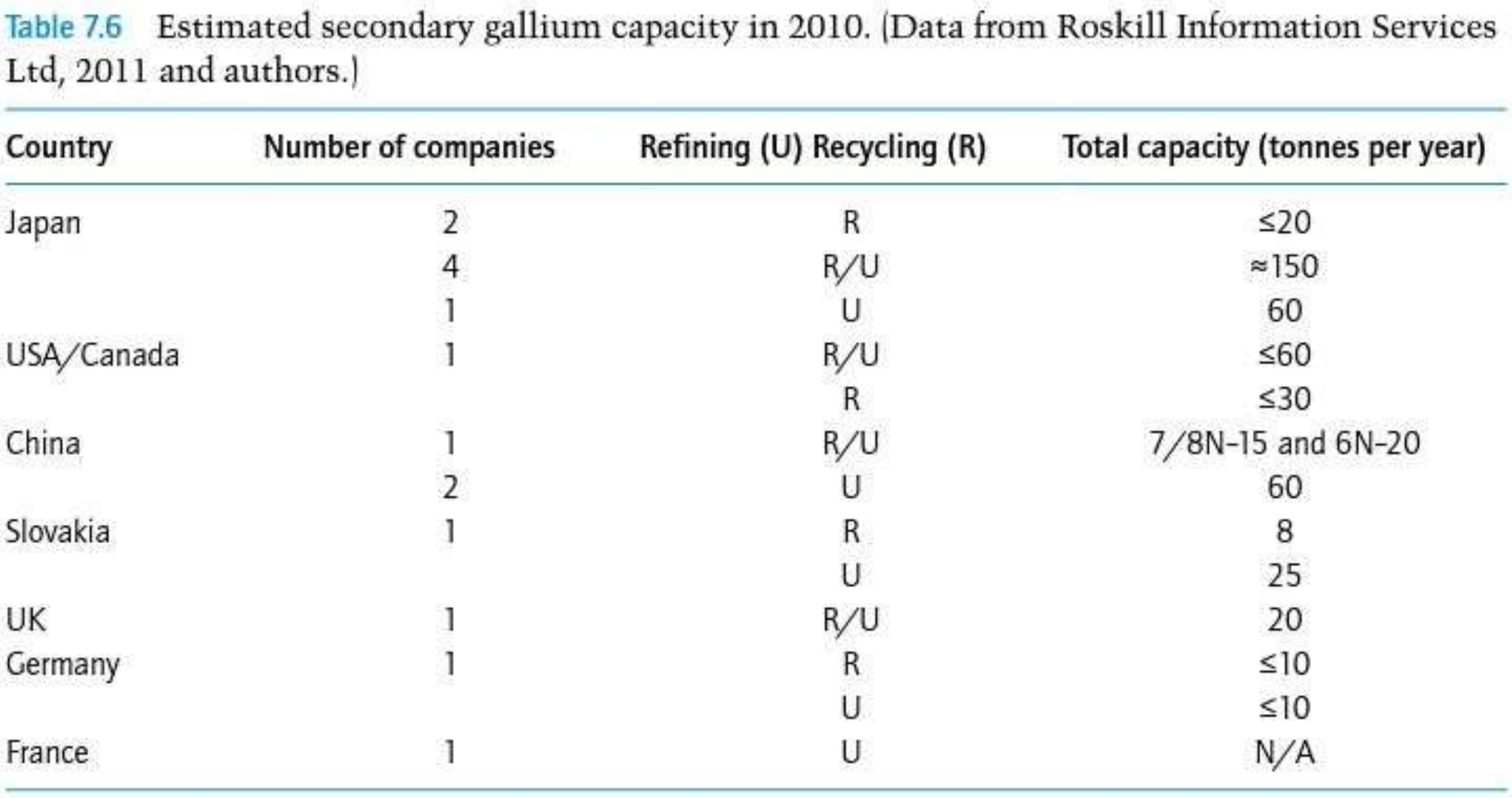


Table 7.6 Estimated secondary gallium capacity in 2010. (Data from Roskill Information Services Ltd, 2011 and authors.)

Country	Number of companies	Refining (U) Recycling (R)	Total capacity (tonnes per year)
Japan	2	R	≤20
	4	R/U	≈150
	1	U	60
USA/Canada	1	R/U	≤60
		R	≤30
China	1	R/U	7/8N-15 and 6N-20
	2	U	60
Slovakia	1	R	8
		U	25
UK	1	R/U	20
Germany	1	R	≤10
		U	≤10
France	1	U	N/A

Ga – prices

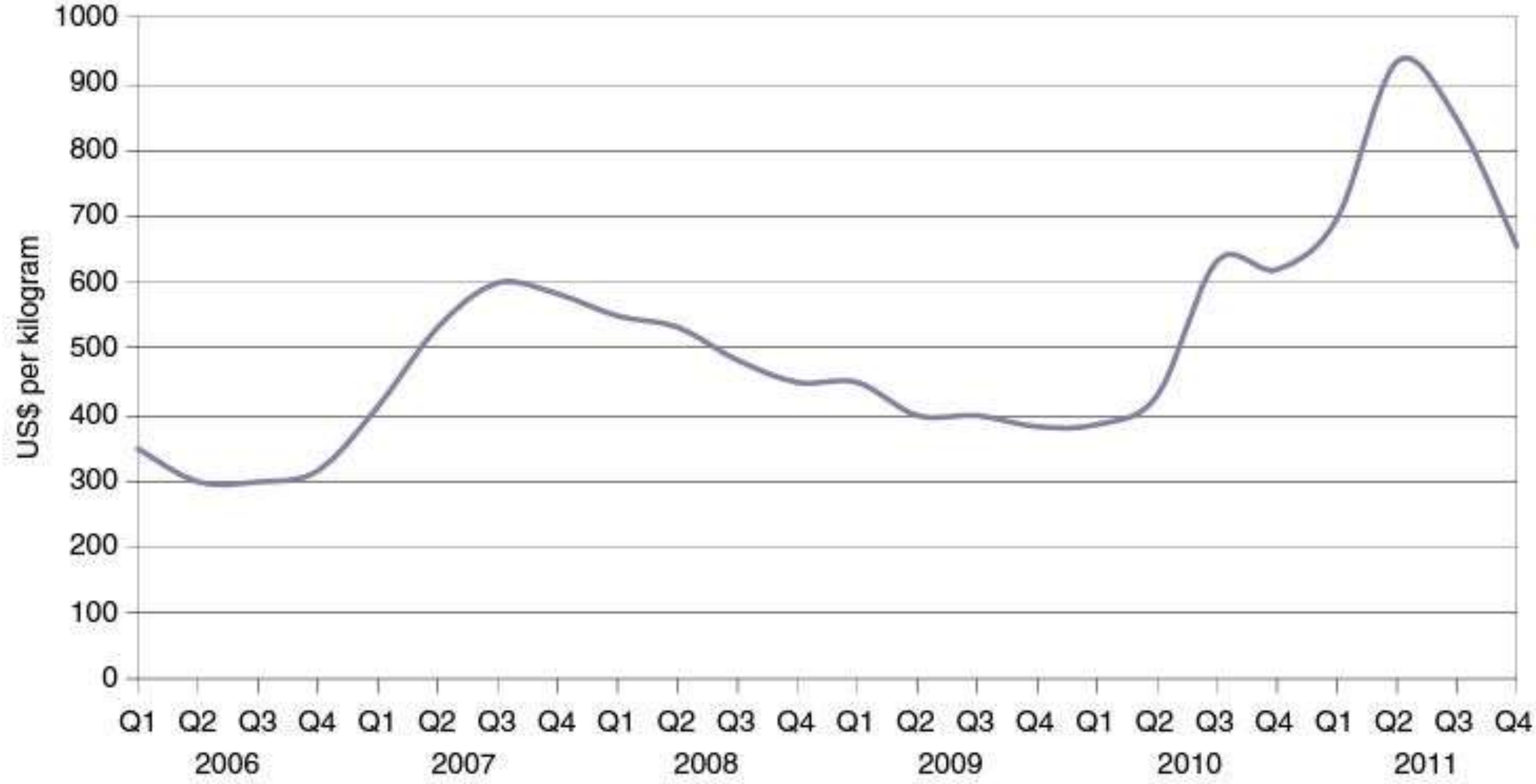


Figure 7.6 Quarterly average prices for gallium metal from January 2006 to November 2011. (Calculated from data quoted in Mining Journal, 2006–2011 and Metal Bulletin, 2011d.)

Ga – environmental issues

- Ga does not occur in nature as a pure metal. As a compound it occurs at trace levels in many areas of the natural environment, including watercourses.

- Acute exposures (ingestion) to certain rare compounds, e.g. **Ga (III) chloride**, can result in throat irritation, breathing difficulties and chest pains.

- **GaAs** is potentially **more toxic to humans** (As).

- **GaN** is non-toxic and potentially suitable for **biomedical implant** applications.

- **Many chemicals** used for the Bayer liquors associated with the production of alumina from bauxite.

- Ga is an essential component of **LEDs**, which are an alternative to traditional incandescent or fluorescent electric lamps.

Ga – outlook

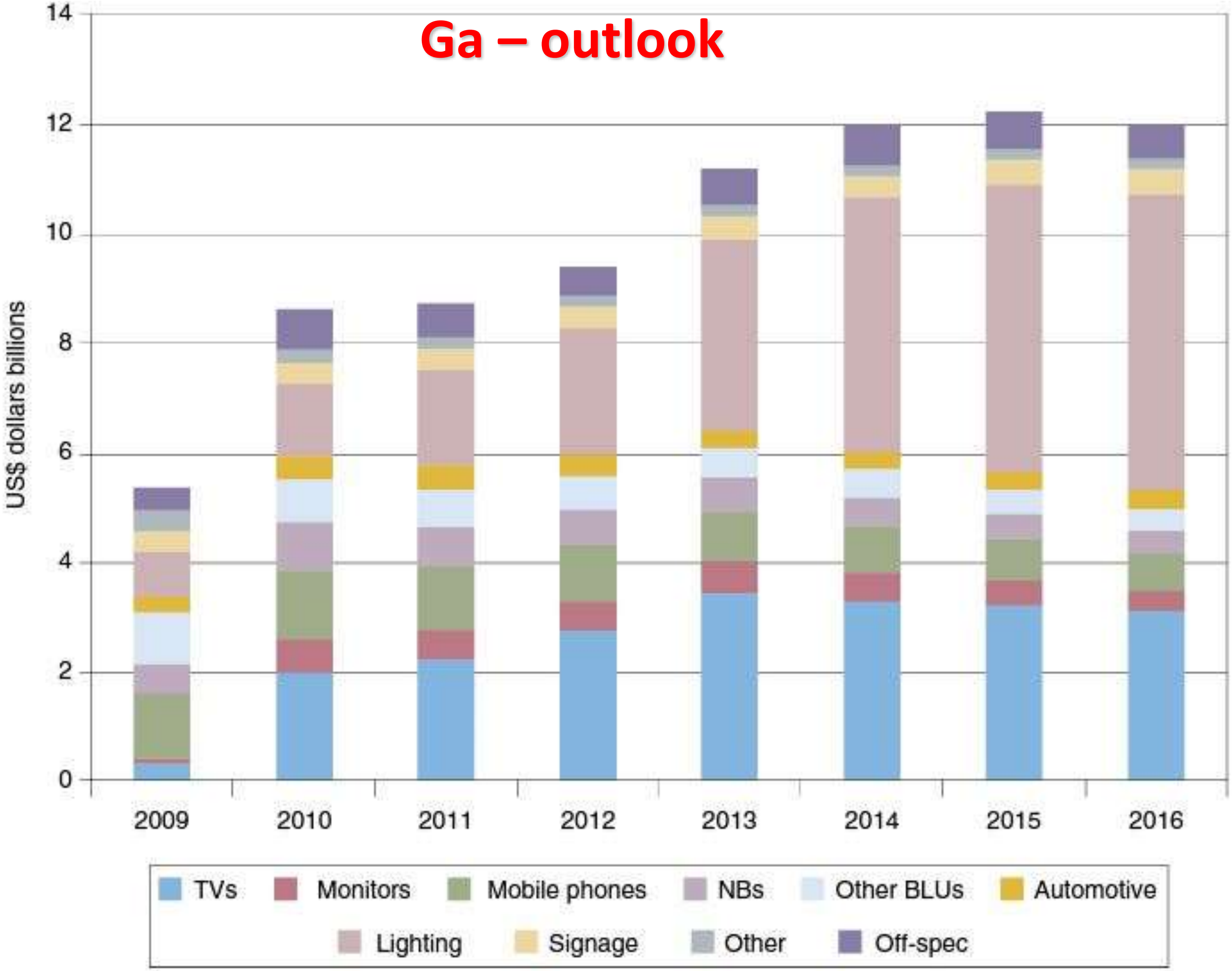
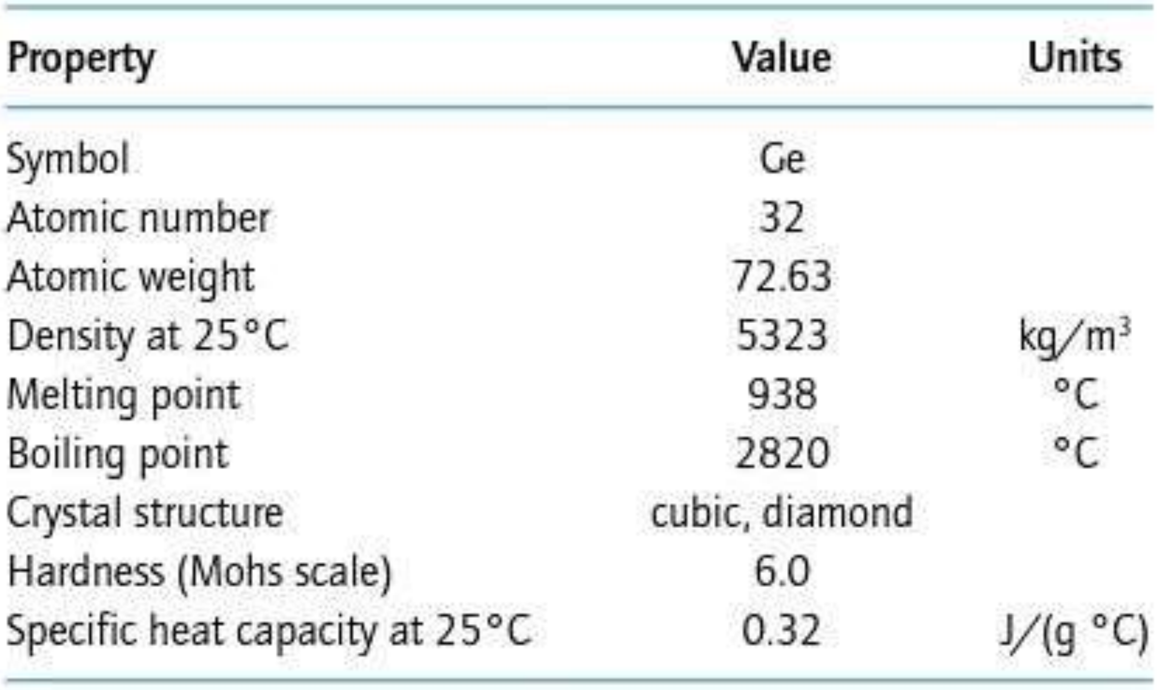


Figure 7.8 Forecast of packaged LEDs by application 2009–2016, revenue by segment. (Data from IMS Research, 2011c.) Notes: TVs, televisions; NBs, notebooks; BLUs, back-lit units.

Germanium

Ge – definitions and characteristics



Property	Value	Units
Symbol	Ge	
Atomic number	32	
Atomic weight	72.63	
Density at 25°C	5323	kg/m^3
Melting point	938	°C
Boiling point	2820	°C
Crystal structure	cubic, diamond	
Hardness (Mohs scale)	6.0	
Specific heat capacity at 25°C	0.32	J/(g °C)

Ge was discovered in **1886** as a component of the mineral argyrodite (Ag_8GeS_6) in silver ores.

Typically, Ge is recovered as a **by-product** from **Zn and Cu ores** and **coal**.

Ge is a greyish-white, brittle semi-metal (**metalloid**). Its electrical properties are those of a **semiconductor**, i.e. between a metal and an insulator, which makes Ge useful for many technical applications.

The oxidation states of Ge are **+2** and **+4**, with a strong tendency towards **quadrivalence**.

Ge – abundance in the Earth and mineralogy

Name	Formula	Typical Ge content (%)	Appearance	Crystal structure	Type locality
Argyrodite	Ag_8GeS_6	5-7	steel grey with red tint, tarnishes black	orthorhombic, pseudocubic	Freiberg, Germany
Canfieldite	$Ag_8(Sn,Ge)(S,Te)_6$	1-2	steel grey with reddish tint, tarnishes black	orthorhombic, pseudocubic	Colquechaca, Bolivia
Briartite	$Cu_2(Fe,Zn)GeS_4$	13-18	grey to grey-blue in reflected light	tetragonal	Kipushi, DR Congo
Reniérite	$(Cu,Zn)_{11}Fe_2(Ge,As)_2S_{16}$	4-8	orange-bronze, tarnishes reddish	tetragonal	Kipushi, DR Congo
Germanite	$Cu_{13}Fe_2Ge_2S_{16}$	5-9	reddish grey, tarnishes dark brown	cubic	Tsumeb, Namibia

- Ge has 5 naturally occurring isotopes, ^{70}Ge, ^{72}Ge, ^{73}Ge, **^{74}Ge** (the most common isotope) and **^{76}Ge**, the latter being slightly radioactive. **^{72}Ge**, when bombarded with alpha particles, will generate stable ^{77}Se, releasing high-energy electrons → used in combination with Rn for **nuclear batteries**.

- **Clarke: 1.5 – 1.6 ppm** (highest enrichment in deep-sea clays ≈ 2 ppm; coal and coal ashes ≈ 2.2 – 15 ppm). **Siderophile**, **lithophile**, **chalcophile** and **organophile** characters. Considerable concentrations of Ge may be found in **Cu-Zn-Fe-Ag sulfides** (up to 3000 ppm in sphalerite) and **sulfosalts**, as well as in association with **organic matter**.

Ge ores and minerals

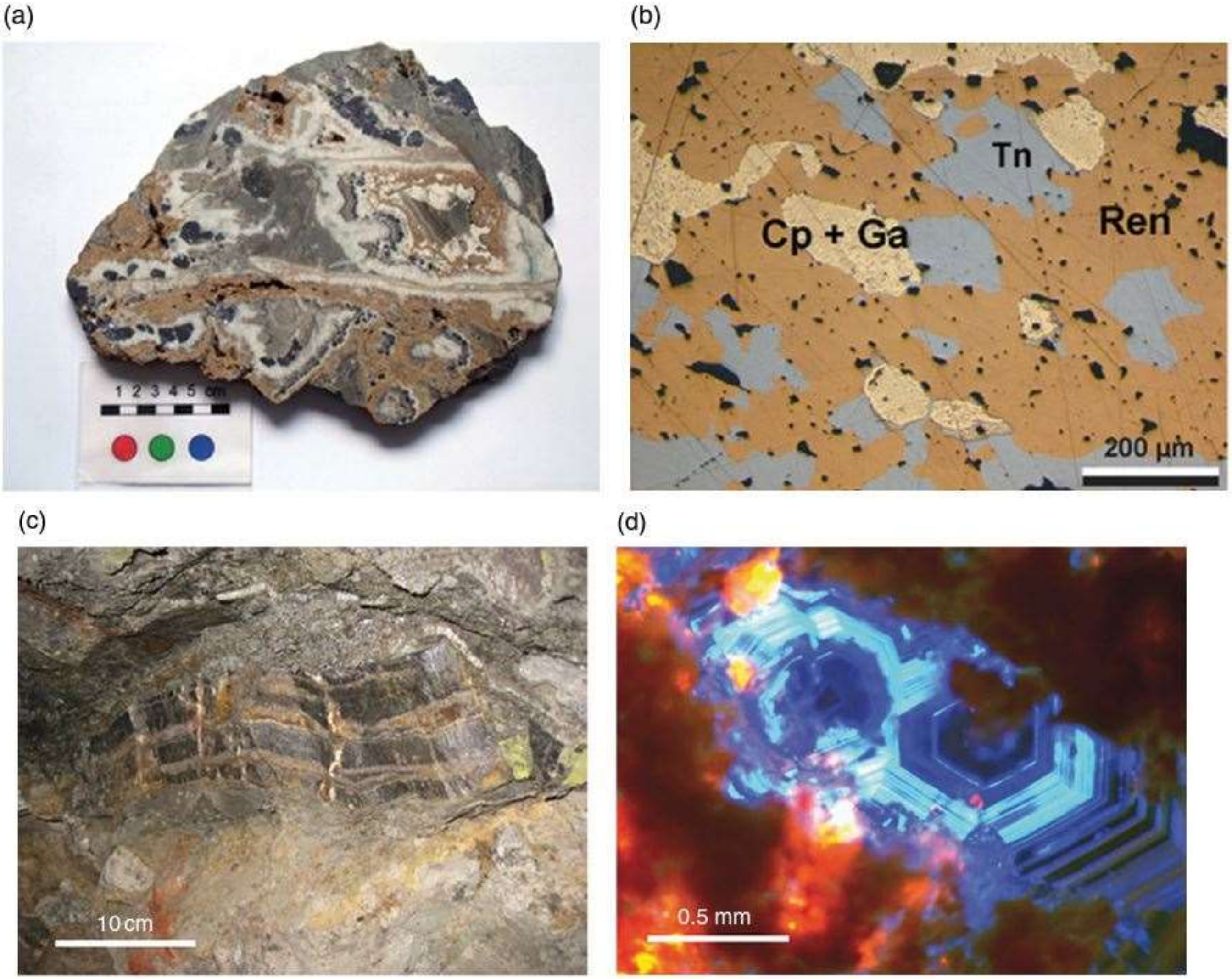


Figure 8.1 Photographs of germanium ores and minerals. (a) Solution collapse breccia cemented by different stages of sphalerite (different shades of brown) and galena (black) from the Bleiberg mine, Austria; grey colour is carbonate host rock, white colour is hydrothermal calcite. This represents a typical carbonate-hosted zinc-lead deposit of the 'Alpine type' grading 200–300 ppm Ge. (Courtesy of W. Prochaska, Leoben.) (b) Germanium ore from the Kipushi deposit, consisting of reniérite (Ren), tennantite (Tn), chalcopyrite (Cp) and gallite $CuGaS_2$ (Ga), forming myrmekitic intergrowth textures in chalcopyrite. Reflected light, oil immersion. (c) Banded Ge-rich sphalerite (grey to black with dark brown interlayers) at the Tres Marias mine, Mexico. Scale bar = 10 cm; photo taken in 2006. (d) Willemite ($ZnSiO_4$) carrying up to 1.5 wt% Ge from Tres Marias, Mexico, showing a bright blue luminescence colour in areas of low trace element concentrations, and weak colours in areas of high trace elements (Ge, Pb). Cathodoluminescence image. Scale bar = 0.5 mm.

Ge concentrations and potential in various deposit types

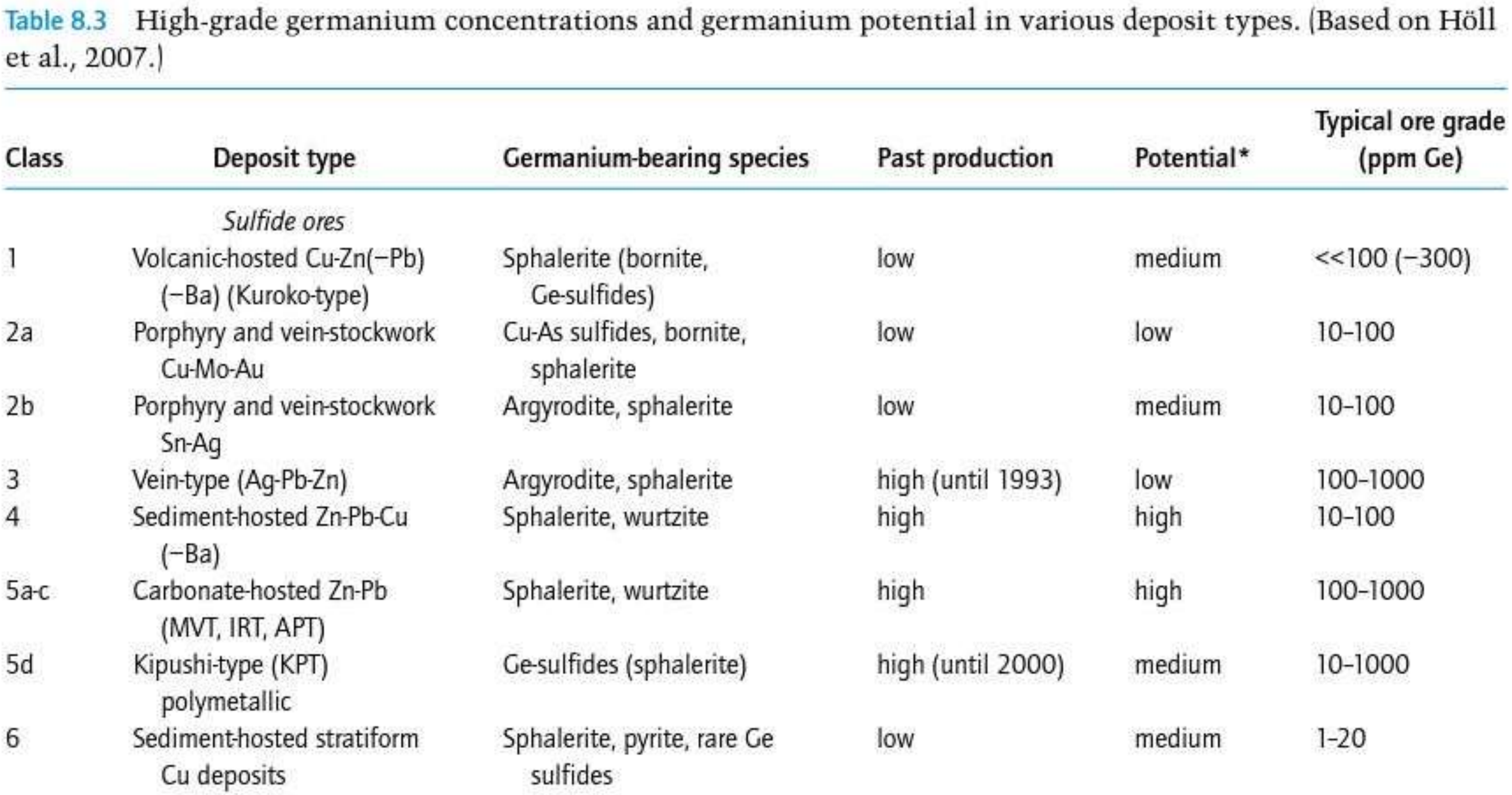


Table 8.3 High-grade germanium concentrations and germanium potential in various deposit types. (Based on Höll et al., 2007.)

Class	Deposit type	Germanium-bearing species	Past production	Potential*	Typical ore grade (ppm Ge)
	Sulfide ores				
1	Volcanic-hosted Cu-Zn(−Pb) (−Ba) (Kuroko-type)	Sphalerite (bornite, Ge-sulfides)	low	medium	<<100 (−300)
2a	Porphyry and vein-stockwork Cu-Mo-Au	Cu-As sulfides, bornite, sphalerite	low	low	10–100
2b	Porphyry and vein-stockwork Sn-Ag	Argyrodite, sphalerite	low	medium	10–100
3	Vein-type (Ag-Pb-Zn)	Argyrodite, sphalerite	high (until 1993)	low	100–1000
4	Sediment-hosted Zn-Pb-Cu (−Ba)	Sphalerite, wurtzite	high	high	10–100
5a-c	Carbonate-hosted Zn-Pb (MVT, IRT, APT)	Sphalerite, wurtzite	high	high	100–1000
5d	Kipushi-type (KPT) polymetallic	Ge-sulfides (sphalerite)	high (until 2000)	medium	10–1000
6	Sediment-hosted stratiform Cu deposits	Sphalerite, pyrite, rare Ge sulfides	low	medium	1–20

Ge concentrations and potential in various deposit types

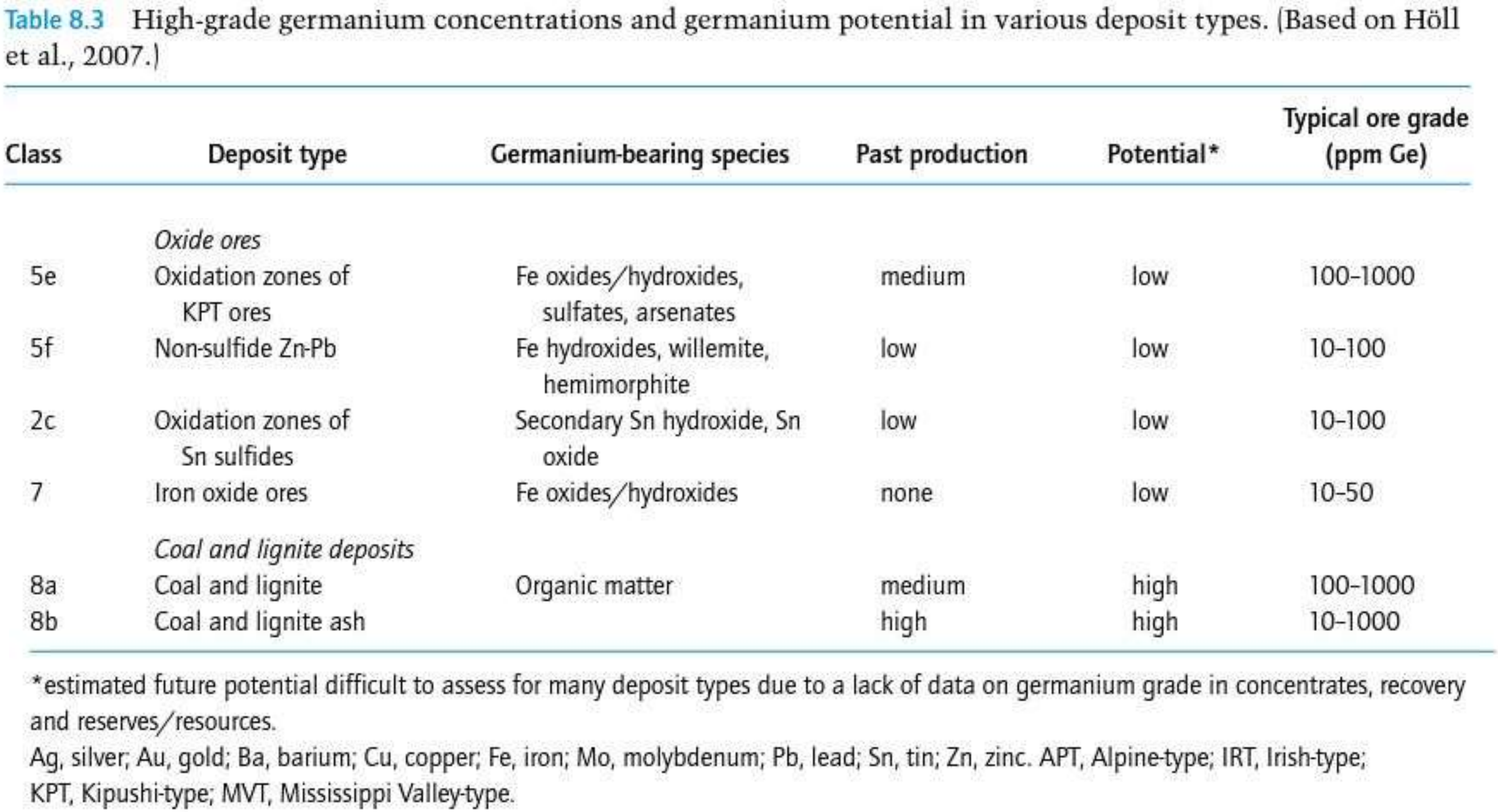


Table 8.3 High-grade germanium concentrations and germanium potential in various deposit types. (Based on Höll et al., 2007.)

Class	Deposit type	Germanium-bearing species	Past production	Potential*	Typical ore grade (ppm Ge)
	Oxide ores				
5e	Oxidation zones of KPT ores	Fe oxides/hydroxides, sulfates, arsenates	medium	low	100–1000
5f	Non-sulfide Zn-Pb	Fe hydroxides, willemite, hemimorphite	low	low	10–100
2c	Oxidation zones of Sn sulfides	Secondary Sn hydroxide, Sn oxide	low	low	10–100
7	Iron oxide ores	Fe oxides/hydroxides	none	low	10–50
	Coal and lignite deposits				
8a	Coal and lignite	Organic matter	medium	high	100–1000
8b	Coal and lignite ash		high	high	10–1000

*estimated future potential difficult to assess for many deposit types due to a lack of data on germanium grade in concentrates, recovery and reserves/resources.

Ag, silver; Au, gold; Ba, barium; Cu, copper; Fe, iron; Mo, molybdenum; Pb, lead; Sn, tin; Zn, zinc. APT, Alpine-type; IRT, Irish-type; KPT, Kipushi-type; MVT, Mississippi Valley-type.

Ge – global distribution of mines and major occurrences

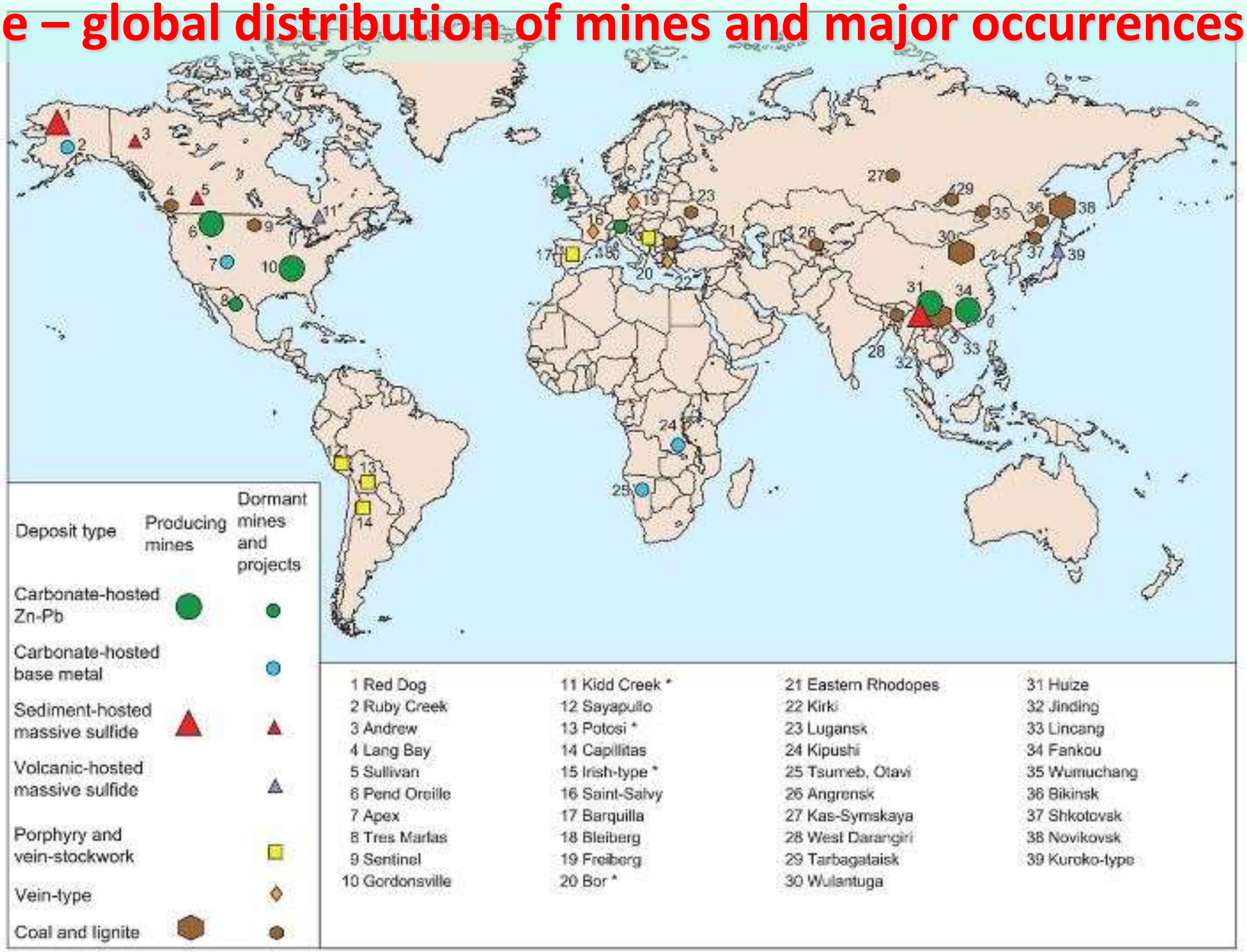


Figure 8.2 The global distribution of mines, deposits and major occurrences from which germanium may be produced. Locations marked * are producing mines where the deposit contains germanium, but which are not currently recovering the germanium.

Ge – extraction methods and processing

- Ge is a by-product in some sulfide ores and in some coals (surface and underground mining methods).

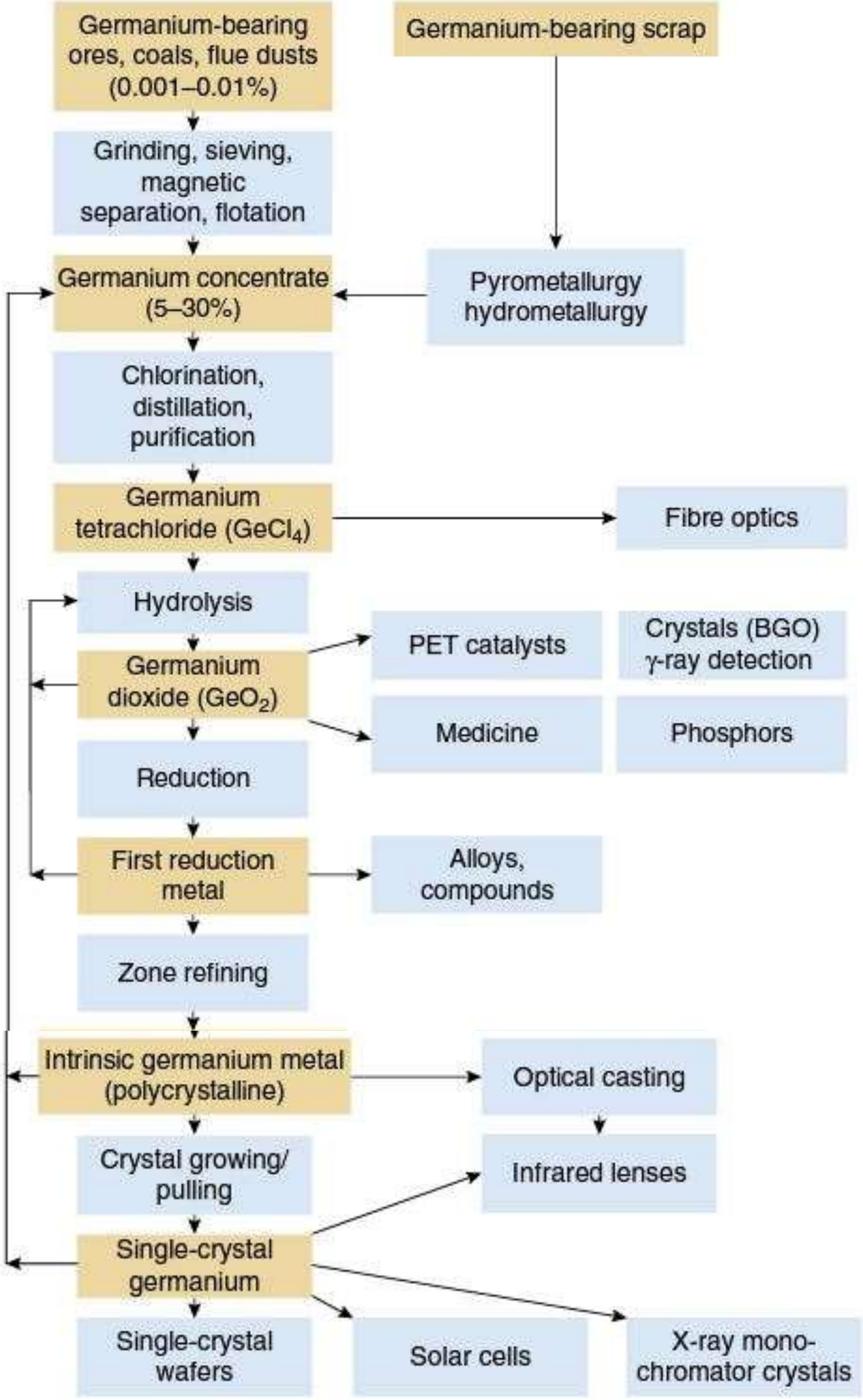


Figure 8.3 Simplified germanium processing flow diagram. (BGO, bismuth germanium oxides ($Bi_4Ge_3O_{12}$); PET, polyethylene teraphthalate.) (Based on Butterman and Jorgenson, 2005 and Naumov, 2007.)

Ge – specifications and uses

Ge is used and traded in a variety of forms:

- **$GeCl_4$**: optical fibres.
- **GeO_2** : catalyst for PET, phosphors.
- **Ge single crystals**: optical components in infrared optical systems and electronics.

USES:

- Ge is an intrinsic **semiconductor**, particularly effective at high frequencies and low voltages;
- It is **transparent to infrared light**;
- It is a **glass-former**;
- It has a **high refractive index**;
- It has **low chromatic dispersion**;
- It has an ability to **catalyse the polymerization** in the production of plastic.

Gamma ray detectors, X-ray monochromators, thermo-photovoltaics, medical and metallurgical applications.

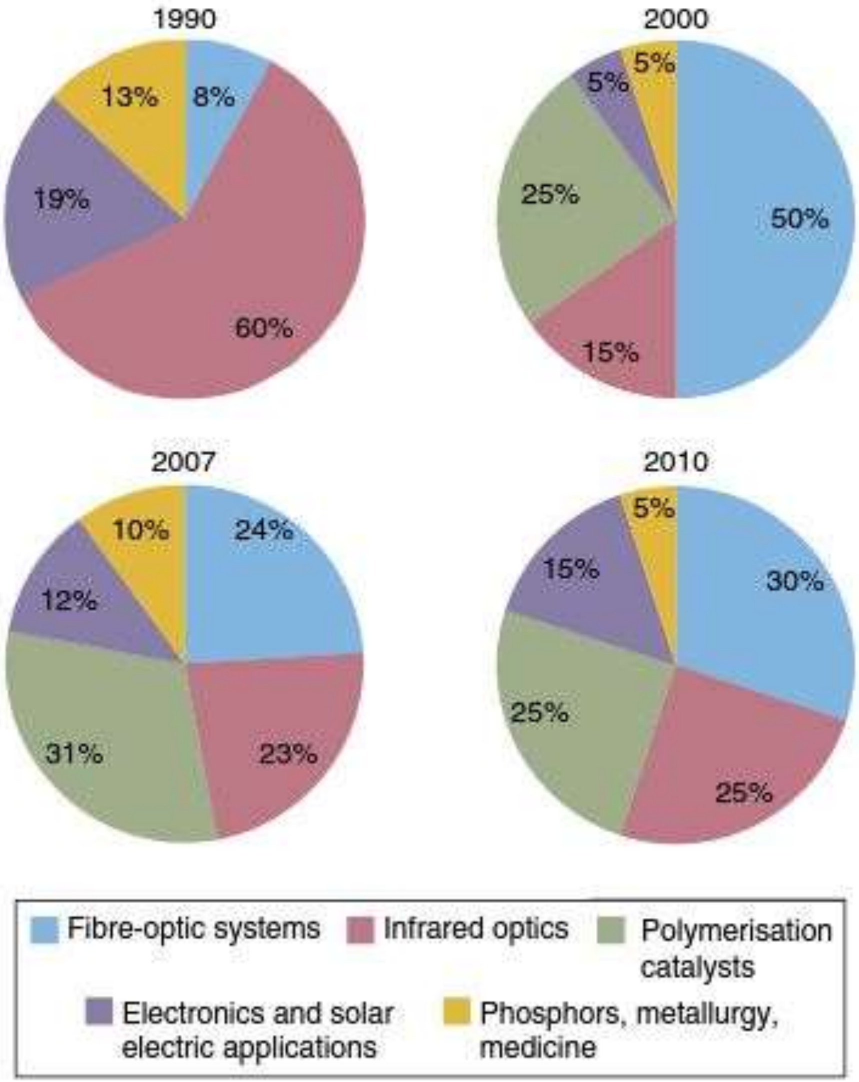


Figure 8.4 Comparison of global end-uses of germanium in 1990, 2000, 2007 and 2010. (Data from Guberman, 2011.)

Ge – major uses

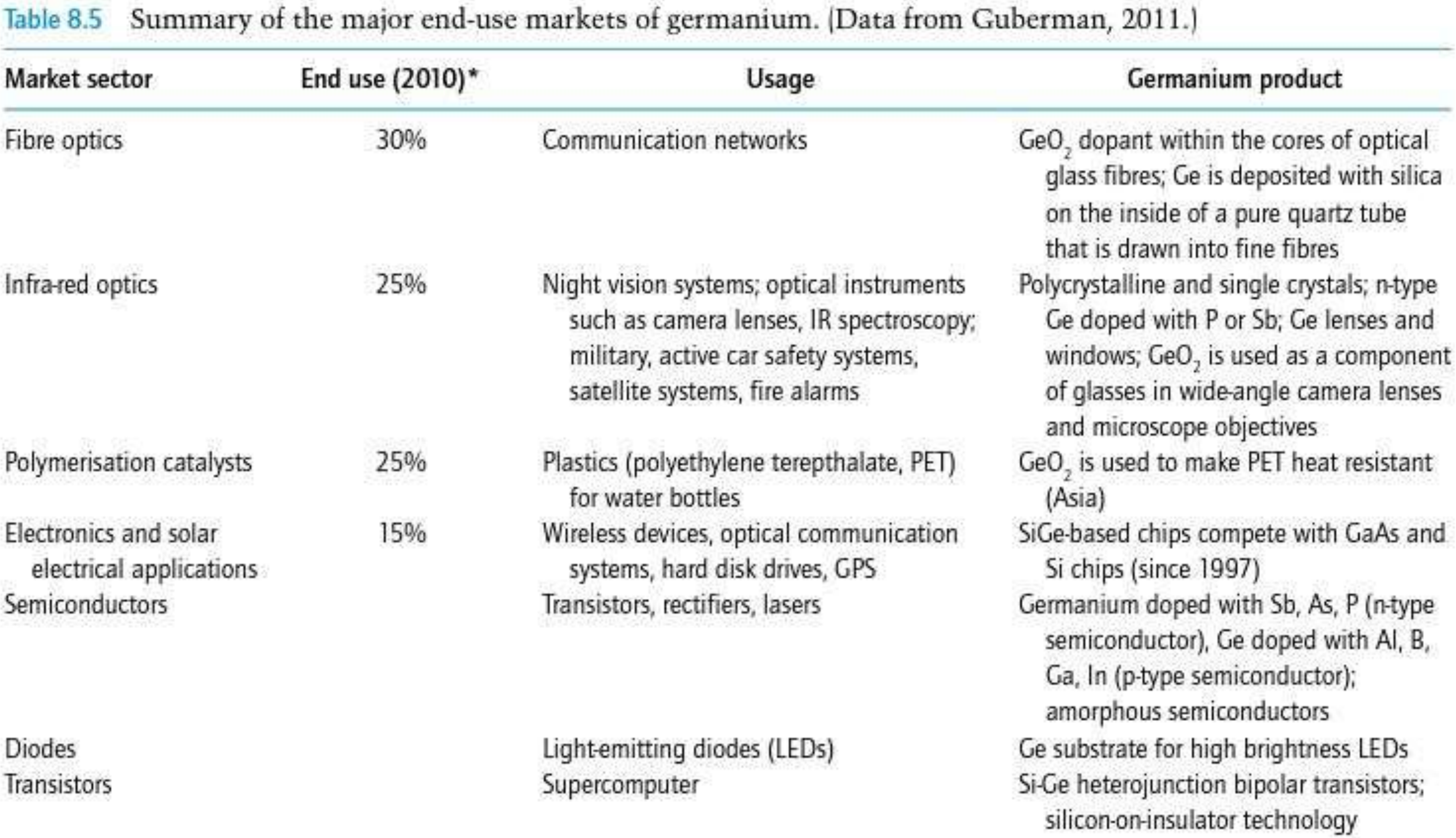


Table 8.5 Summary of the major end-use markets of germanium. (Data from Guberman, 2011.)

Market sector	End use (2010)*	Usage	Germanium product
Fibre optics	30%	Communication networks	GeO_2 dopant within the cores of optical glass fibres; Ge is deposited with silica on the inside of a pure quartz tube that is drawn into fine fibres
Infra-red optics	25%	Night vision systems; optical instruments such as camera lenses, IR spectroscopy; military, active car safety systems, satellite systems, fire alarms	Polycrystalline and single crystals; n-type Ge doped with P or Sb; Ge lenses and windows; GeO_2 is used as a component of glasses in wide-angle camera lenses and microscope objectives
Polymerisation catalysts	25%	Plastics (polyethylene terepthalate, PET) for water bottles	GeO_2 is used to make PET heat resistant (Asia)
Electronics and solar electrical applications	15%	Wireless devices, optical communication systems, hard disk drives, GPS	SiGe-based chips compete with GaAs and Si chips (since 1997)
Semiconductors		Transistors, rectifiers, lasers	Germanium doped with Sb, As, P (n-type semiconductor), Ge doped with Al, B, Ga, In (p-type semiconductor); amorphous semiconductors
Diodes		Light-emitting diodes (LEDs)	Ge substrate for high brightness LEDs
Transistors		Supercomputer	Si-Ge heterojunction bipolar transistors; silicon-on-insulator technology

Ge – major uses

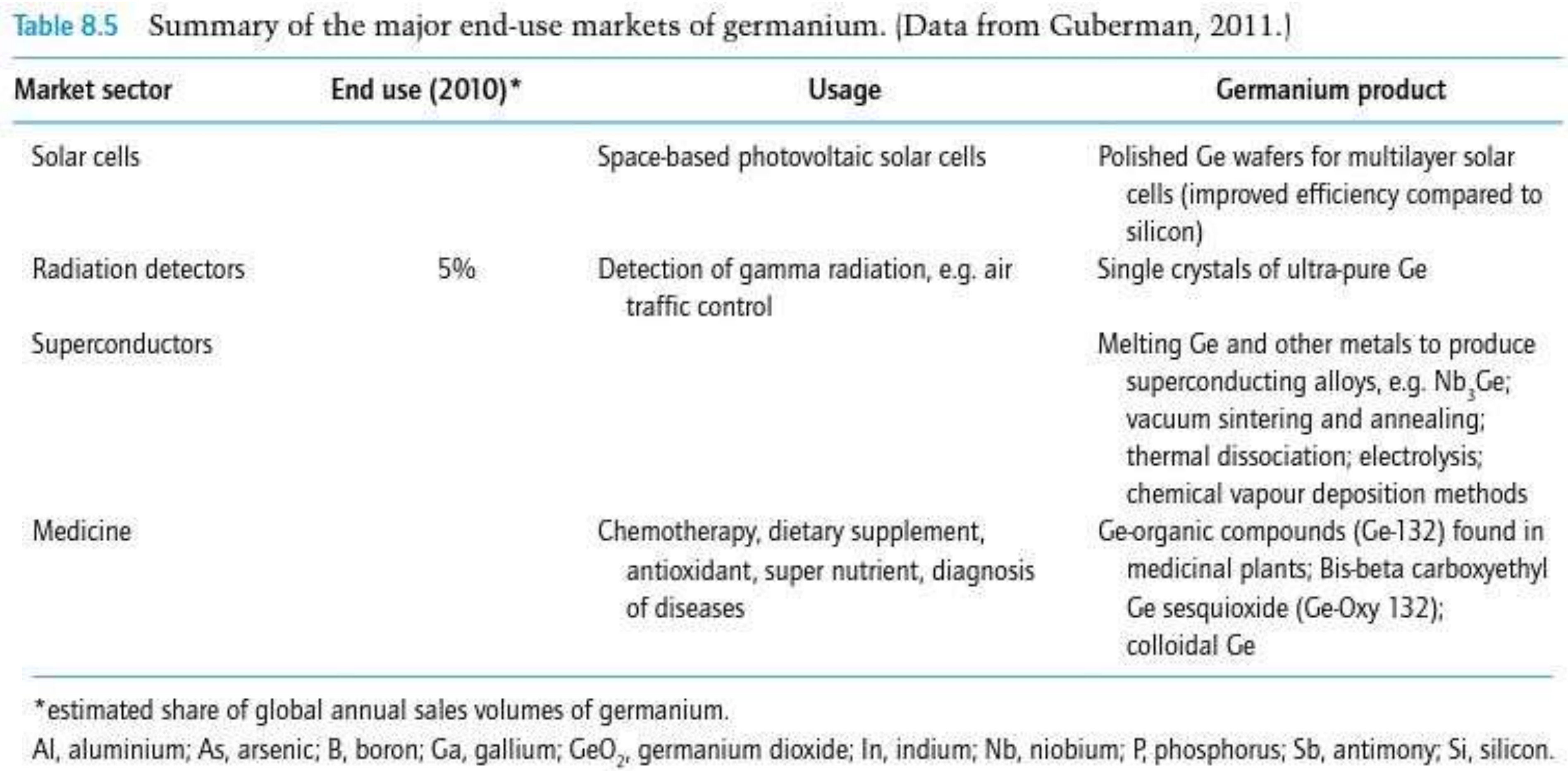


Table 8.5 Summary of the major end-use markets of germanium. (Data from Guberman, 2011.)

Market sector	End use (2010)*	Usage	Germanium product
Solar cells		Space-based photovoltaic solar cells	Polished Ge wafers for multilayer solar cells (improved efficiency compared to silicon)
Radiation detectors	5%	Detection of gamma radiation, e.g. air traffic control	Single crystals of ultra-pure Ge
Superconductors			Melting Ge and other metals to produce superconducting alloys, e.g. Nb_3Ge; vacuum sintering and annealing; thermal dissociation; electrolysis; chemical vapour deposition methods
Medicine		Chemotherapy, dietary supplement, antioxidant, super nutrient, diagnosis of diseases	Ge-organic compounds (Ge-132) found in medicinal plants; Bis-beta carboxyethyl Ge sesquioxide (Ge-Oxy 132); colloidal Ge

*estimated share of global annual sales volumes of germanium.

Al, aluminium; As, arsenic; B, boron; Ga, gallium; GeO_2, germanium dioxide; In, indium; Nb, niobium; P, phosphorus; Sb, antimony; Si, silicon.

Ge – recycling and substitution

- **Recycling**
  - Due to its **dispersion** in most products and application in very low quantities, little Ge is recovered from post-consumer scrap (“old scrap”). Recycling from “new scrap”, however, is more widespread in the production of **Ge-containing fibre-optic** cables and **infrared imaging devices**.

  - Most of the scrap is sent to Ge processors for recycling which are able to recycle material containing a minimum of 2% Ge.

  - On a global scale, about **25-35%** of the total Ge used is processed from recycled scrap, mainly “new scrap”.

- **Substitution**
  - **Fibre-optic applications**: Zr-In-based fluoride glass (research at an early stage).

  - **Electronic applications:** Si, ZnSe, GASIR (infrared-transmitting chalcogenide glass).

  - **PET**: Ti, Sb and Al-based catalysts.

  - **Solar cells**: Inverted Metamorphic Cells, GaAs, GaP.

Ge – active and potential producers from sulfide ores

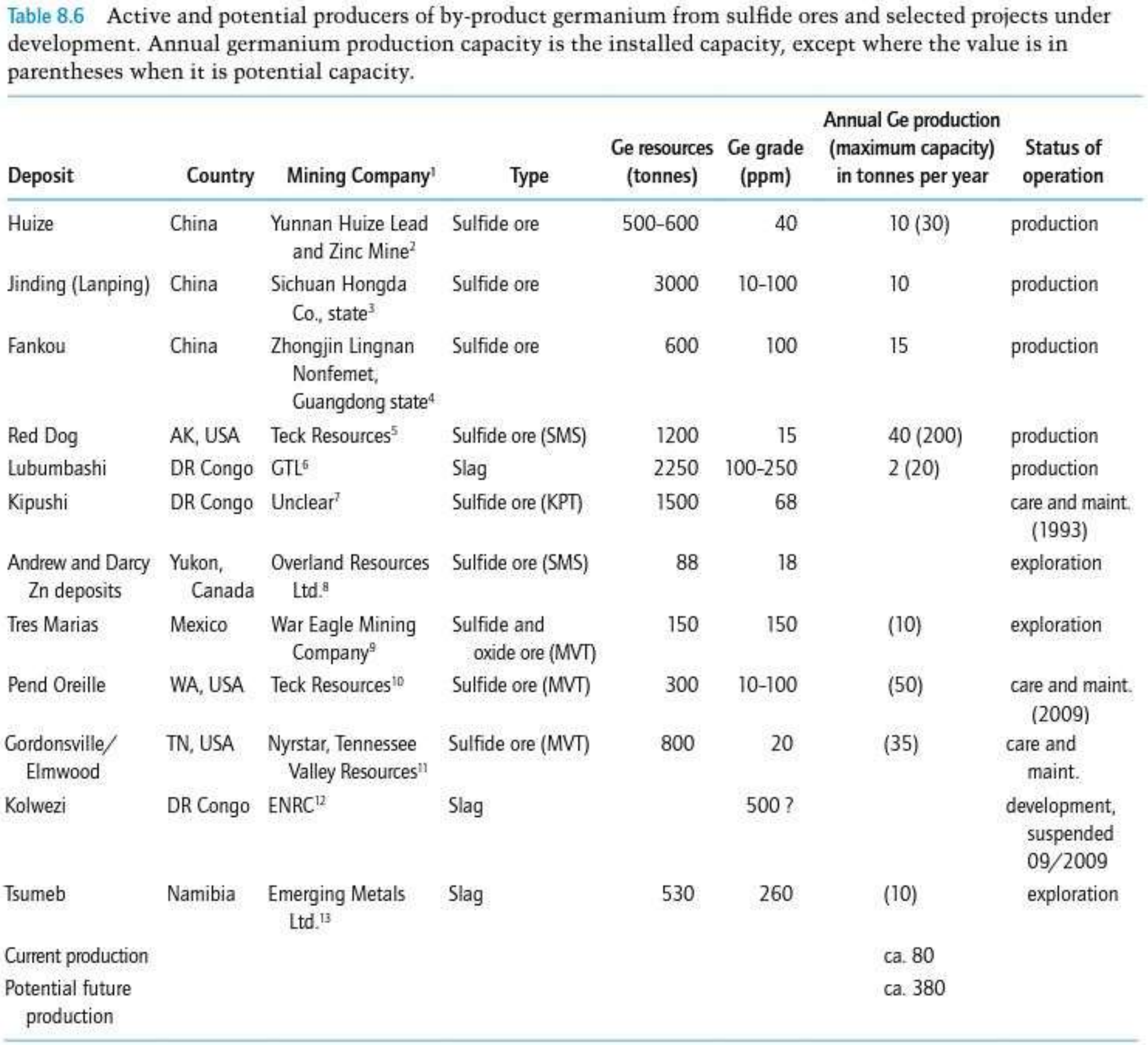


Table 8.6 Active and potential producers of by-product germanium from sulfide ores and selected projects under development. Annual germanium production capacity is the installed capacity, except where the value is in parentheses when it is potential capacity.

Deposit	Country	Mining Company[1]	Type	Ge resources (tonnes)	Ge grade (ppm)	Annual Ge production (maximum capacity) in tonnes per year	Status of operation
Huize	China	Yunnan Huize Lead and Zinc Mine[2]	Sulfide ore	500–600	40	10 (30)	production
Jinding (Lanping)	China	Sichuan Hongda Co., state[3]	Sulfide ore	3000	10–100	10	production
Fankou	China	Zhongjin Lingnan Nonfemet, Guangdong state[4]	Sulfide ore	600	100	15	production
Red Dog	AK, USA	Teck Resources[5]	Sulfide ore (SMS)	1200	15	40 (200)	production
Lubumbashi	DR Congo	GTL[6]	Slag	2250	100–250	2 (20)	production
Kipushi	DR Congo	Unclear[7]	Sulfide ore (KPT)	1500	68		care and maint. (1993)
Andrew and Darcy Zn deposits	Yukon, Canada	Overland Resources Ltd.[8]	Sulfide ore (SMS)	88	18		exploration
Tres Marias	Mexico	War Eagle Mining Company[9]	Sulfide and oxide ore (MVT)	150	150	(10)	exploration
Pend Oreille	WA, USA	Teck Resources[10]	Sulfide ore (MVT)	300	10–100	(50)	care and maint. (2009)
Gordonsville/ Elmwood	TN, USA	Nyrstar, Tennessee Valley Resources[11]	Sulfide ore (MVT)	800	20	(35)	care and maint.
Kolwezi	DR Congo	ENRC[12]	Slag		500 ?		development, suspended 09/2009
Tsumeb	Namibia	Emerging Metals Ltd.[13]	Slag	530	260	(10)	exploration
Current production						ca. 80	
Potential future production						ca. 380	

Ge – producers from Ge-rich lignite and coal

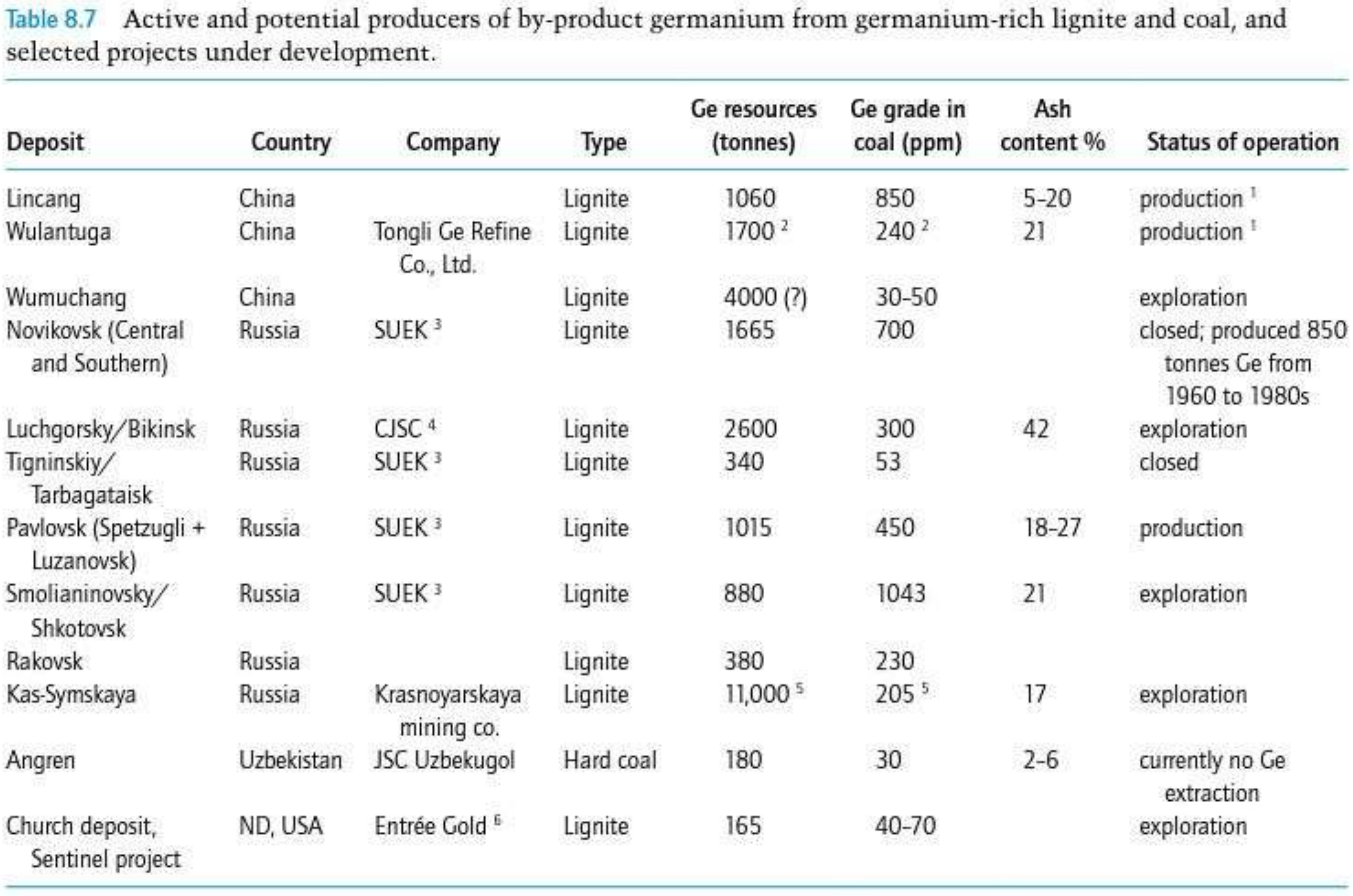


Table 8.7 Active and potential producers of by-product germanium from germanium-rich lignite and coal, and selected projects under development.

Deposit	Country	Company	Type	Ge resources (tonnes)	Ge grade in coal (ppm)	Ash content %	Status of operation
Lincang	China		Lignite	1060	850	5-20	production [1]
Wulantuga	China	Tongli Ge Refine Co., Ltd.	Lignite	1700 [2]	240 [2]	21	production [1]
Wumuchang	China		Lignite	4000 (?)	30-50		exploration
Novikovsk (Central and Southern)	Russia	SUEK [3]	Lignite	1665	700		closed; produced 850 tonnes Ge from 1960 to 1980s
Luchgorsky/Bikinsk	Russia	CJSC [4]	Lignite	2600	300	42	exploration
Tigninskiy/ Tarbagataisk	Russia	SUEK [3]	Lignite	340	53		closed
Pavlovsk (Spetzugli + Luzanovsk)	Russia	SUEK [3]	Lignite	1015	450	18-27	production
Smolianinovsky/ Shkotovsk	Russia	SUEK [3]	Lignite	880	1043	21	exploration
Rakovsk	Russia		Lignite	380	230		
Kas-Symskaya	Russia	Krasnoyarskaya mining co.	Lignite	11,000 [5]	205 [5]	17	exploration
Angren	Uzbekistan	JSC Uzbekugol	Hard coal	180	30	2-6	currently no Ge extraction
Church deposit, Sentinel project	ND, USA	Entrée Gold [6]	Lignite	165	40-70		exploration

Ge – world production

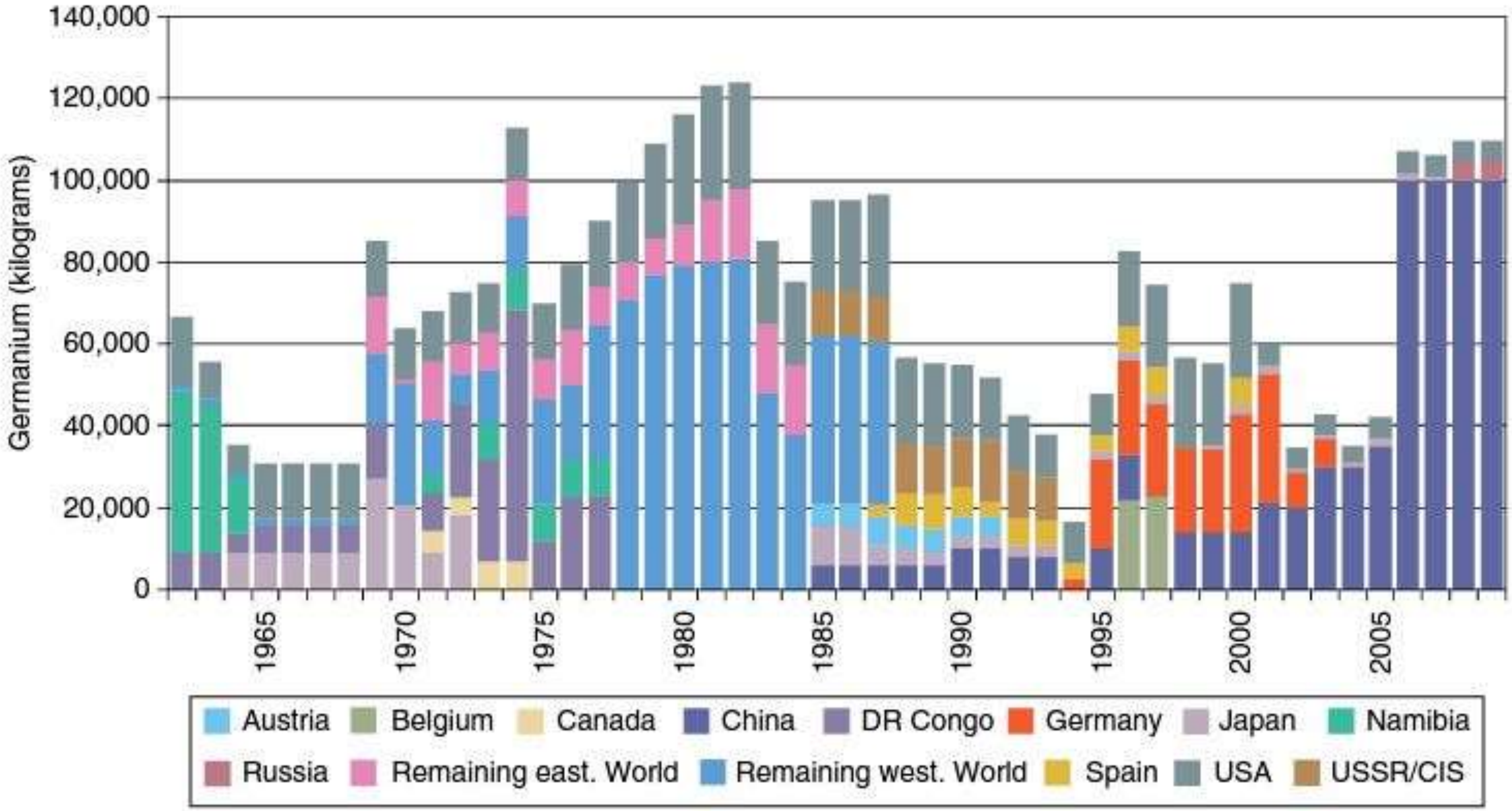


Figure 8.5 World germanium production, by country, 1962–2009. (Data from BGR database.)

Ge – prices

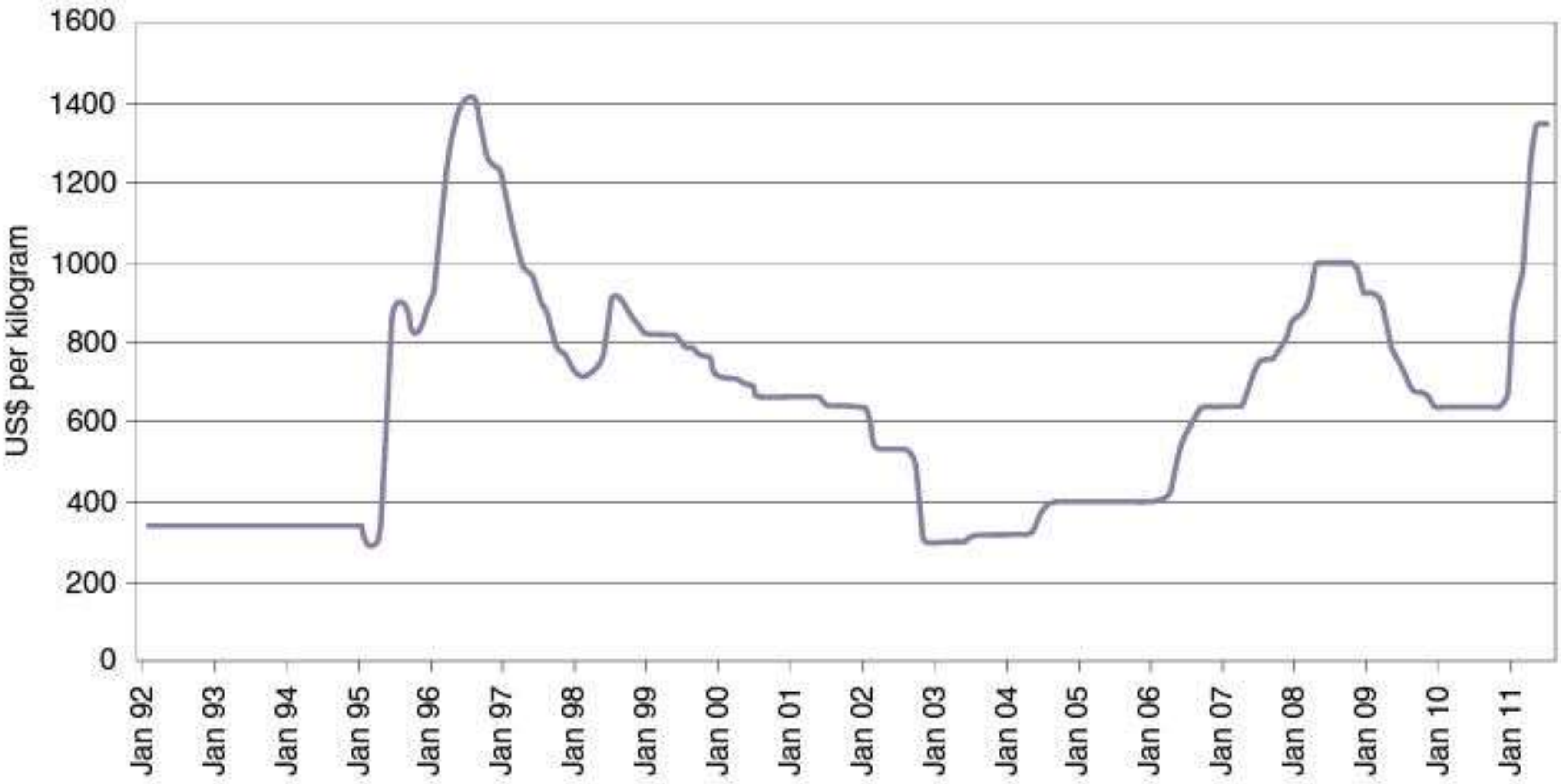


Figure 8.6 Germanium dioxide price (minimum 99.99%, monthly averages), 1992–2011. (Data from BGR database, 2012.)

Ge – environmental issues

- Ge has little or no effect upon the environment (trace element in rocks).

- During processing of Ge-bearing materials, **As** and **Cd** may present potential problems.

- Ge compounds also have a low order of toxicity, except for **Ge tetrahydride**, which is considered toxic.

Major Germanium Applications

1. Infrared Optics
2. Optical Fibre
3. PET Catalyst
4. Solar Cells

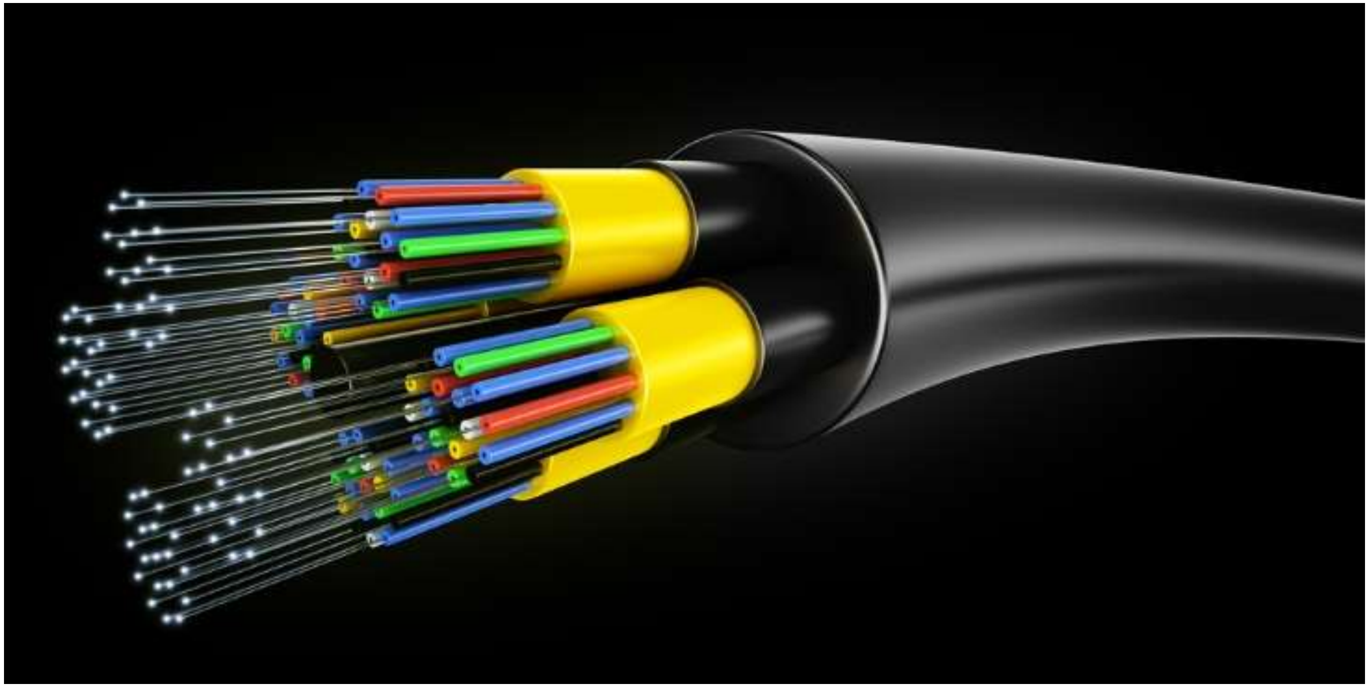
Major Germanium Producers

1. China
2. USA
3. Canada

Ge – outlook

- **Supply challenges:** major Ge supply will be driven by **primary Zn mine** production, and by extraction from **coal ashes**. Recycling of old scrap will not be a significant contribution to world supply.

- **Demand drivers**: **fibre optics**, future **infrared optic applications** (e.g. car safety systems), **electronics** (detectors, transistors and semiconductors), high-end **LEDs**, GeSbTe optical discs.



Indium

In – definitions and characteristics

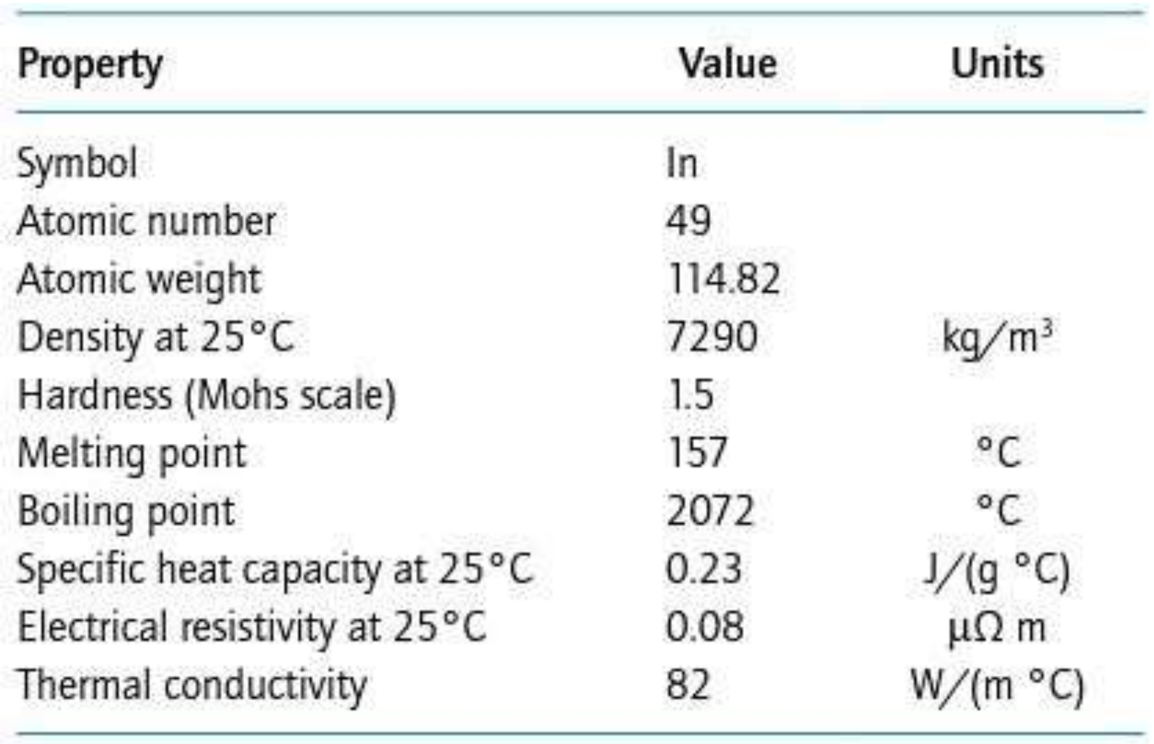
In was discovered in **1863** by two German chemists, who were testing zinc ores. They named it “*indium*” from the indigo blue colour seen in its spectrum.

In 1924, In was found to have a valuable ability to **stabilize non-ferrous metals**.

The early applications of In were in **light-emitting diodes** and in coating **bearings** in aircraft engines.

In-containing **semiconductors** became important from the 1950s onwards, while the widespread use of In-containing **nuclear control rods** increased during the 1970s.

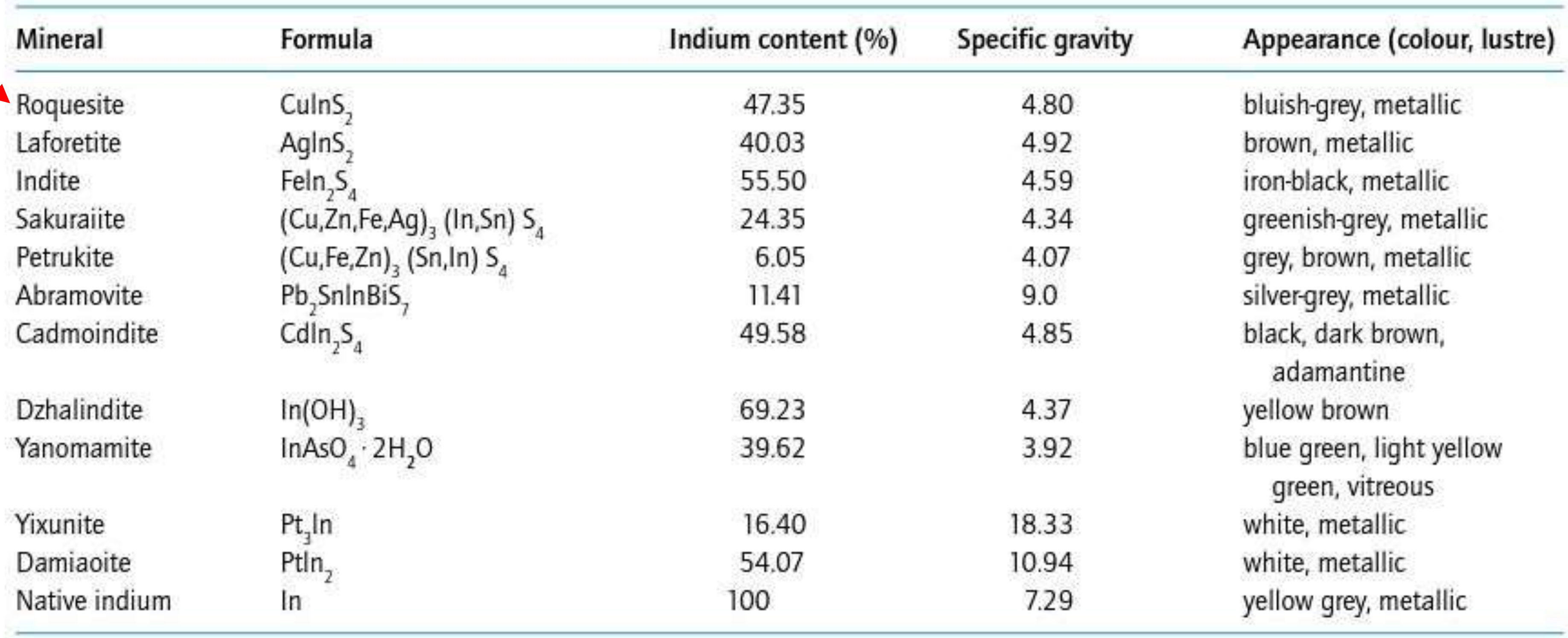
Since 1992 the major application of In has been in the form of In-Sn oxide (ITO) in **liquid-crystal displays**.



Property	Value	Units
Symbol	In	
Atomic number	49	
Atomic weight	114.82	
Density at 25°C	7290	kg/m^3
Hardness (Mohs scale)	1.5	
Melting point	157	°C
Boiling point	2072	°C
Specific heat capacity at 25°C	0.23	J/(g °C)
Electrical resistivity at 25°C	0.08	μΩ m
Thermal conductivity	82	W/(m °C)

- In is a soft, lustrous, silver-white metal, **very malleable** and **ductile** and retains these properties at **very low T** approaching absolute zero, making it ideal for cryogenic and vacuum applications. In does not workharden and is easily cold-welded.
- On heating, In reacts directly with metalloids (As, Sb, Se, Te) ad with halogens, S and P.

In – abundance in the Earth and mineralogy



Mineral	Formula	Indium content (%)	Specific gravity	Appearance (colour, lustre)
Roquesite	$CuInS_2$	47.35	4.80	bluish-grey, metallic
Laforetite	$AgInS_2$	40.03	4.92	brown, metallic
Indite	$FeIn_2S_4$	55.50	4.59	iron-black, metallic
Sakuraiite	$(Cu,Zn,Fe,Ag)_3 (In,Sn) S_4$	24.35	4.34	greenish-grey, metallic
Petrukite	$(Cu,Fe,Zn)_3 (Sn,In) S_4$	6.05	4.07	grey, brown, metallic
Abramovite	$Pb_2SnInBiS_7$	11.41	9.0	silver-grey, metallic
Cadmoindite	$CdIn_2S_4$	49.58	4.85	black, dark brown, adamantine
Dzhalindite	$In(OH)_3$	69.23	4.37	yellow brown
Yanomamite	$InAsO_4 \cdot 2H_2O$	39.62	3.92	blue green, light yellow green, vitreous
Yixunite	Pt_3In	16.40	18.33	white, metallic
Damiaoite	$PtIn_2$	54.07	10.94	white, metallic
Native indium	In	100	7.29	yellow grey, metallic

- In is a post-transition metal of Group 13 falling between Ga and Tl. The geochemical properties are such that it tends to occur in nature with **base metals** (Cu, Ag, Zn, Cd, Sn, Pb and Bi).
- In has two main oxidation states, **+3 (III)** and **+1 (I)**.
- **Clarke: 0.05 ppm** (continental crust) - **0.072 ppm** (oceanic crust). Seawater: 0.2 – 0.7 ppb.
- In is a highly volatile chalcophile element which behaves in a moderately to highly incompatible manner during mantle melting.
- In minerals are rare, **roquesite** is the most important (trace component in ore minerals like bornite, chalcopyrite and sphalerite). **Sphalerite** is the most important In-bearing mineral.

In – ore

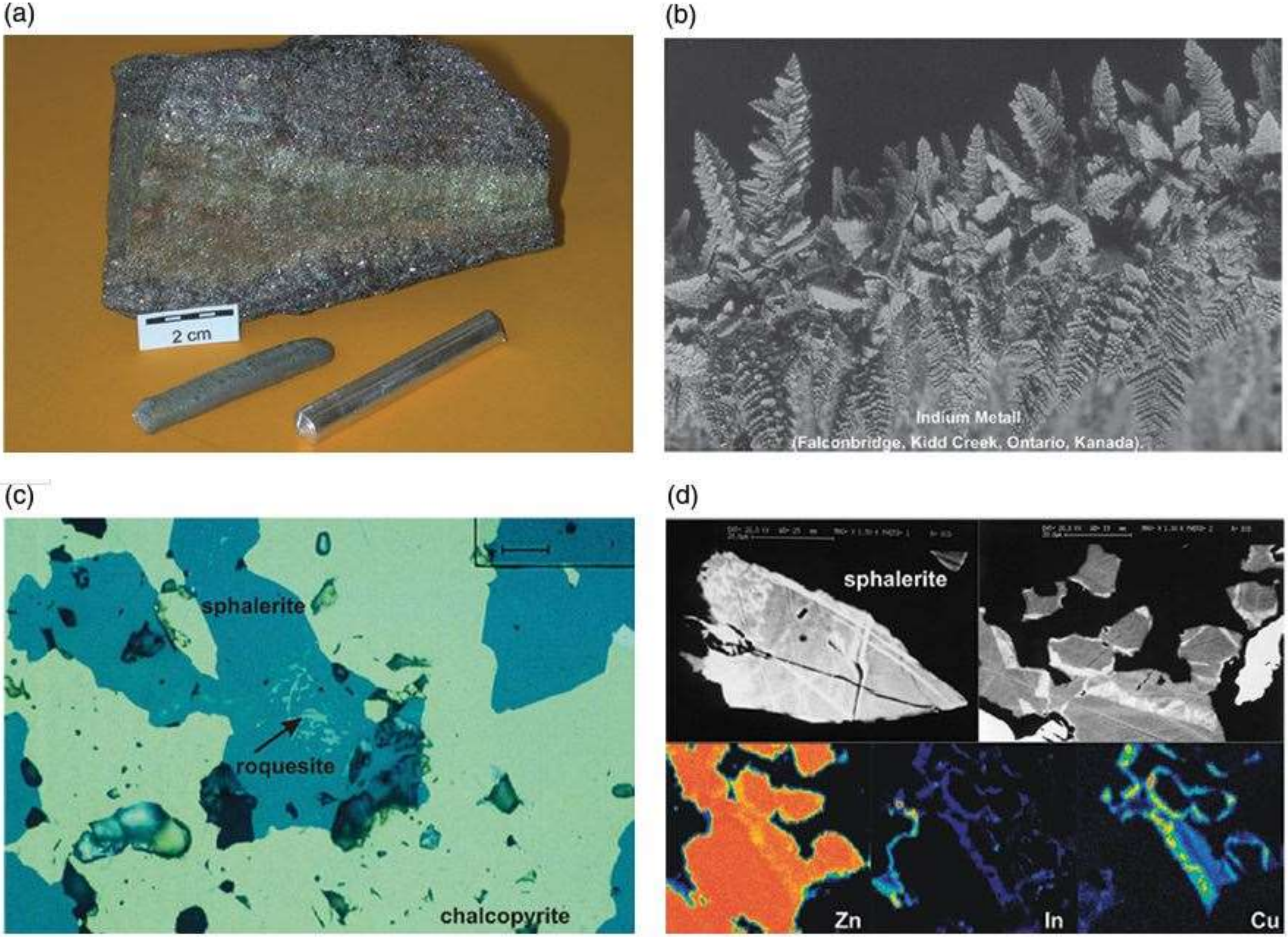


Figure 9.1 (a) Example of indium-rich ore (600 ppm In), Maranda J volcanic-hosted massive sulfide (VHMS) deposit, South Africa and indium rods (99.95% In); (b) Native indium metal from the former Kidd Creek processing plant, Canada (courtesy of Falconbridge Ltd); (c) Chalcopyrite-sphalerite ore with roquesite inclusions in sphalerite; Kidd Creek, Canada; (d) Sphalerite-roquesite solid solution series as light zonal enrichments in sphalerite grains from the Vai Lili hydrothermal vent field, southern Lau basin, south-west Pacific.

In – major deposit classes

- In occurs in **different types** of ore deposits of **all ages**.
- In deposits are most commonly associated with **base-metal hydrothermal** ore-forming systems enriched in Zn, Cu, Pb and Sn, accompanied by trace metals such as Bi, Cd and Ag.
- The most important deposits are **volcanic- and sediment-hosted base-metal sulfide deposits**, characterized by high metal abundance and large tonnages. The concentration of In in these ores is in the range **20 – 200 ppm**.
- The majority of In-bearing ore deposits are associated with the **subduction-related** western Pacific plate boundaries.

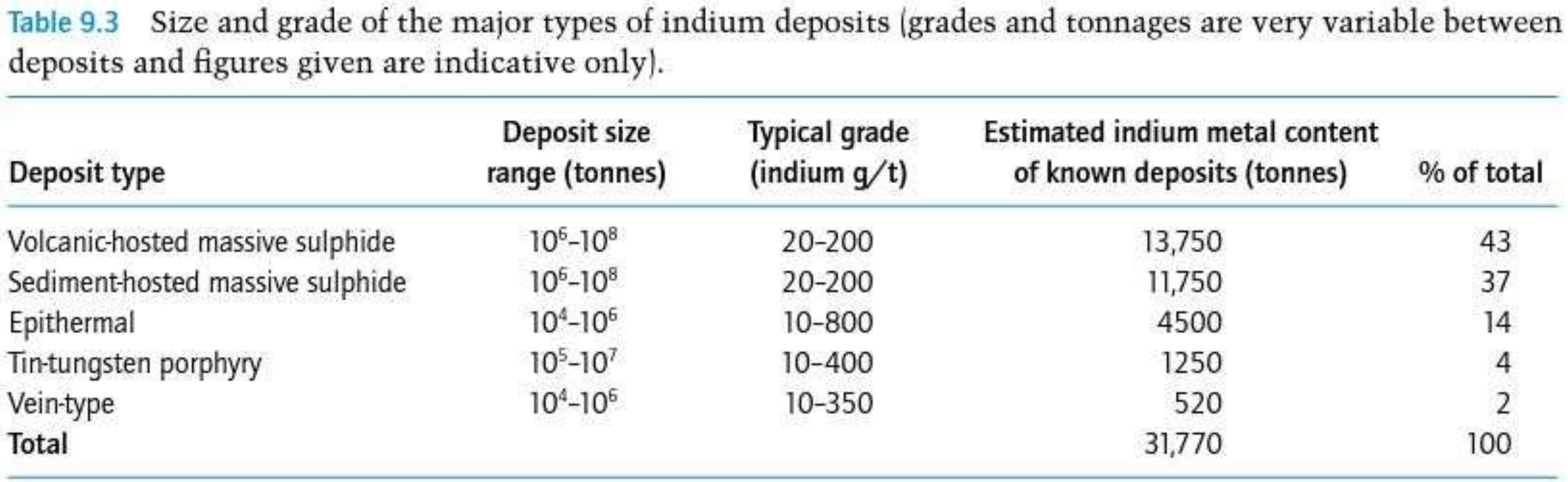
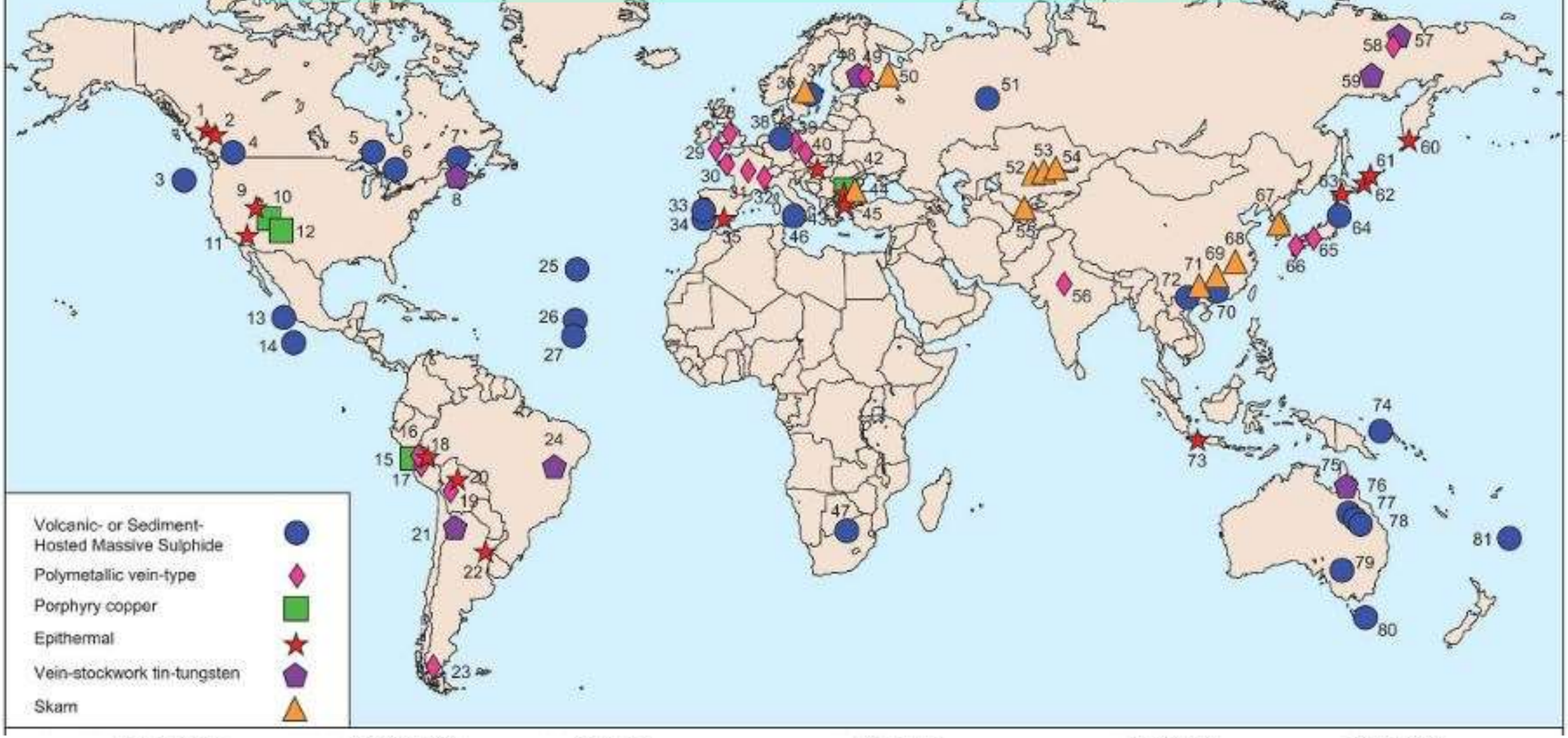


Table 9.3 Size and grade of the major types of indium deposits (grades and tonnages are very variable between deposits and figures given are indicative only).

Deposit type	Deposit size range (tonnes)	Typical grade (indium g/t)	Estimated indium metal content of known deposits (tonnes)	% of total
Volcanic-hosted massive sulphide	10^6–10^8	20–200	13,750	43
Sediment-hosted massive sulphide	10^6–10^8	20–200	11,750	37
Epithermal	10^4–10^6	10–800	4500	14
Tin-tungsten porphyry	10^5–10^7	10–400	1250	4
Vein-type	10^4–10^6	10–350	520	2
Total			31,770	100

In – worldwide deposit distribution



1 Equity Silver
2 Silver Queen
3 Axial seamount
4 Sullivan
5 Geco
6 Kidd Creek
7 Brunswick Camp
8 Mount Pleasant
9 Crypto
10 Bingham
11 McLaughlin
12 Central District
13 East Pacific Rise 21°N
14 East Pacific rise 13°N
15 Cerro de Pasco
16 Carahuacra
17 Sayapullo
18 Morococha
19 Bolivia (9 locations)
20 Malku Khota
21 Pirquitas
22 San Roque, Rio Negro
23 Pinguino, Santa Cruz
24 Mangabeira
25 Broken Spur
26 TAG, Mid Atlantic Ridge
27 Snake pit
28 West Shropshire
29 Cornwall (2 locations)
30 Telhaie
31 Vaulry
32 Charrier (2 locations)
33 Lagoa Salgada
34 Neves-Corvo
35 Cartagena
36 Gåsborn, Bergslagen
37 Långban, Bergslagen
38 Rammelsberg
39 Freiberg (2 locations)
40 Bohemian Massif (7 locations)
41 Nagyborzsony
42 Elacite/Asarel, Sredna Gora
43 Sredna Gora (5 locations)
44 Malko-Tarnovo (6 locations)
45 Kirki
46 Palinuro
47 Murchison (2 locations)
48 Getmossmalmen (4 locations)
49 Jungfrubergen
50 Kitel
51 Southern Urals (6 locations)
52 Kansay
53 Kyzyl Espe (4 locations)
54 Sarykan (3 locations)
55 Karamazar
56 Tosham
57 Deputaskoe
58 Lifudsin
59 Pravourmiiskoe
60 Mutnovsky
61 Kudryavy
62 Prasolov
63 Toyoha (8 locations)
64 Kuroko
65 Akenobe (6 locations)
66 Kyushu (5 locations)
67 Ulsan
68 Qibaoshan
69 Dachang
70 Dachang
71 Gejiu
72 Laochang
73 Merapi
74 Manus Basin
75 Baal Gammon
76 Waterloo
77 Dry River South
78 Balcooma
79 Broken Hill
80 Rosebery
81 Lau Basin

In – extraction methods and processing

The mining methods employed to extract In are related to the recovery of other **base metals** in **massive sulfide deposits**.

The strict **co-enrichment with Zn and Cu** makes Cu-bearing Zn ores the most favorable for In recovery.

In can be recovered also from **Cu** and **Sn ores**.

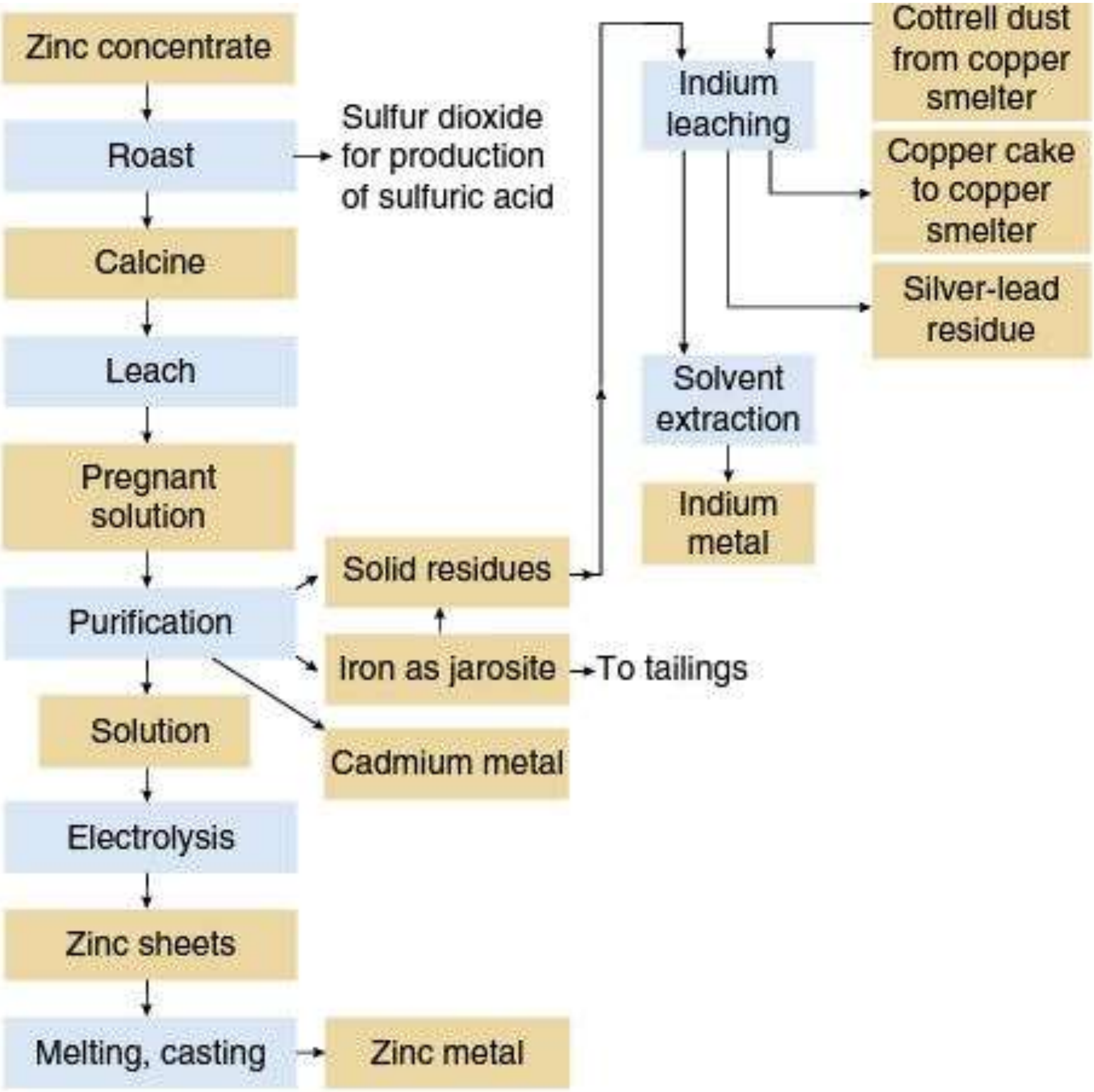


Figure 9.3 Generalised beneficiation flow diagram, based on the Kidd Creek operations. (Modified after http://www.mining-technology.com/projects/kidd_creek/kidd_creek7.html.)

In – specifications and uses

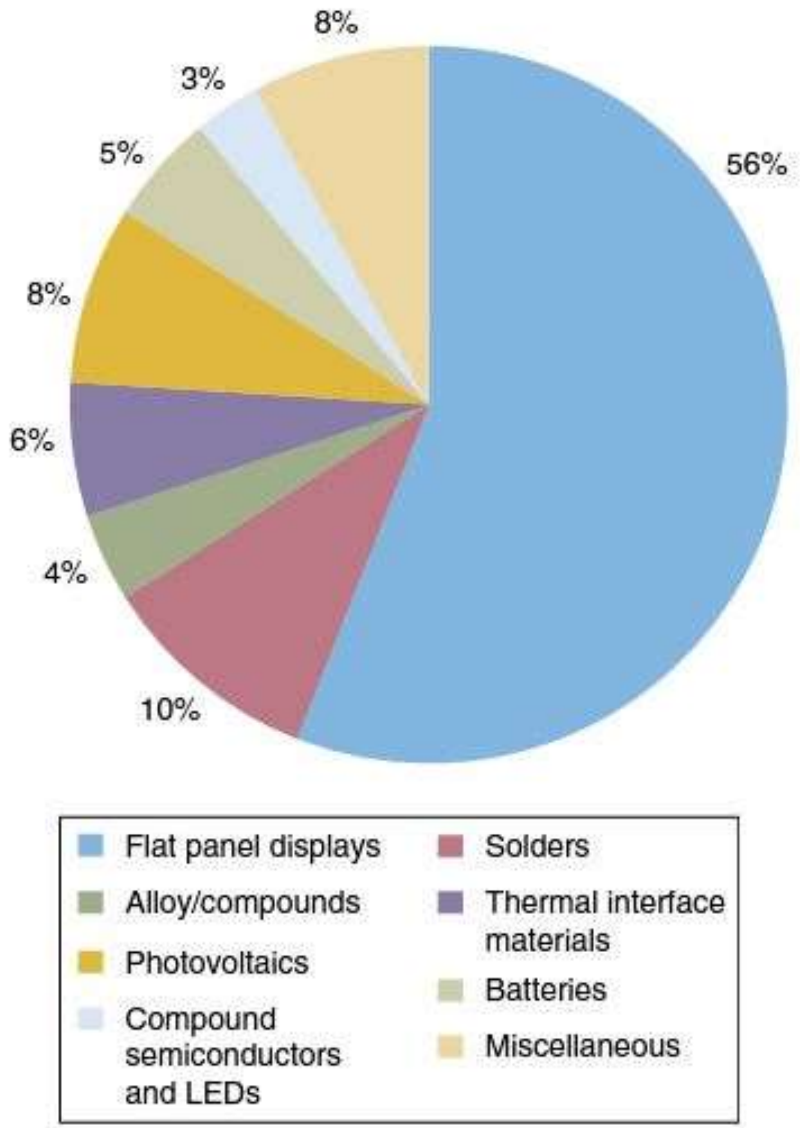


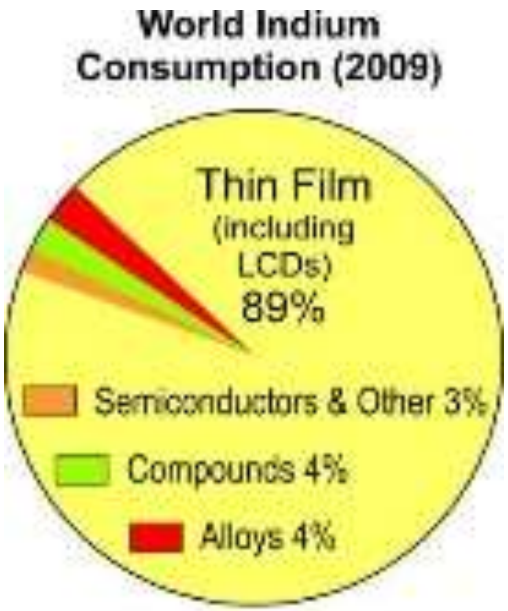
Figure 9.4 The main end-uses of indium in 2010. (Modified after Mikolajczak and Harrower, 2012, courtesy of Indium Corporation.)

In is traded as **In metal** in a wide variety of forms including pellets, powder, plates, sheets, wires and foils. The standard quality is 99.99% (termed “4N”), but higher purities up to 5N and 7N (99.99999%) are also standard specifications.

- **Low melting point**;
- **Workability at very low T** (-273 °C);
- **Suppleness**, softer than Pb;
- **Tight adhesion** to other metals;
- **Dissolution in acids**;
- **Amphoteric** character;
- **No reaction** with H_2O, B, Si or C;
- Reaction with O only **at higher T**;
- Oxidation by halogens or oxalic acids, to give **In (III) compounds**.

In – specifications and uses

- The first large scale application for In was as a **coating for bearings** in high-performance aircraft engines during WW II.
- **Fusible alloys, solder** and **electronics**.
- **Indium-tin oxide (ITO)**: glass coatings, solar collectors, streetlights, electrophoretic, plasma and electroluminescent displays.
- **Alloys and solder**: low melting point alloys with Bi, Sn, Pb and Cd; solders and fusible alloys in the electronic industry. Alloys of Au and Pd used in dentistry often include In. In the nuclear industry an alloy of Ag, In and Cd is used in nuclear control rods.
- **Semiconductors**: photovoltaic industry ($CuInSe_2$, $CuInGaSe_2$ [CIGS], $CuInS_2$ [CIS], $CuInGaS_2$), LEDs, laser diodes, photodetectors.
- **Surface coating**: engine bearings, plating, electrodeless lamps, thermal interface material in PCs.


World Indium Consumption (2009)

Adapted from data of AIM Specialty Materials

In – recycling and substitution

- **Recycling**

  - The recovery of In from production waste (“new scrap”) and, to a lesser extent, from recycling of In-bearing electronic scrap have become increasingly important in the last decade. **About 2/3 (1000 t) of global In supply comes from recycling**.

  - Most **ITO** producing countries have increased their recycling rates significantly.

- **Substitution**

  - **ITO**: Sb-Sn oxide, Zn oxide with Al doping (AZO), carbon nanotube, poly(3,4-ethylene dioxythiophene).

  - **Semiconductors:** Ga arsenide.

In – resources and reserves

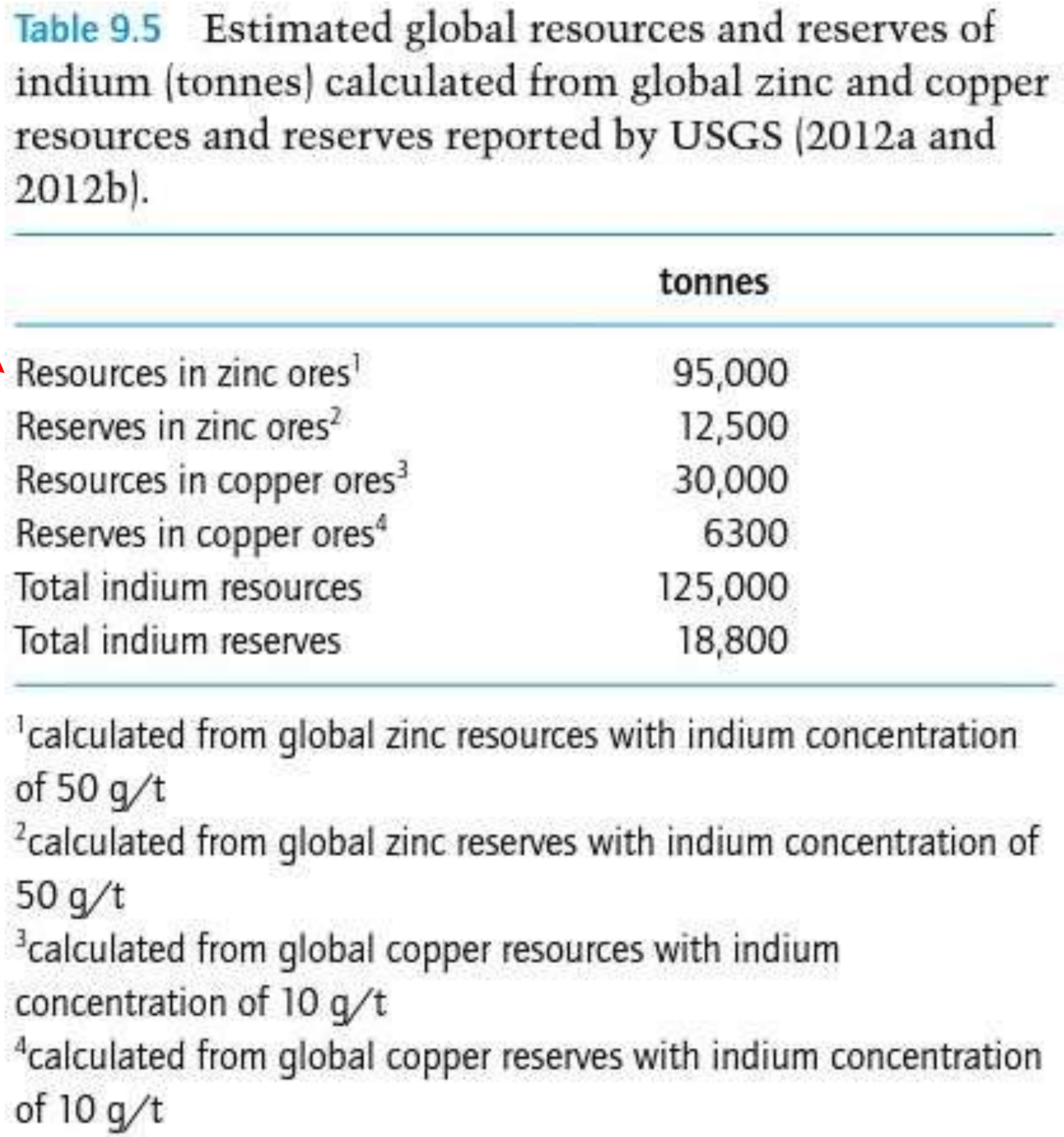


Table 9.5 Estimated global resources and reserves of indium (tonnes) calculated from global zinc and copper resources and reserves reported by USGS (2012a and 2012b).

	tonnes
Resources in zinc ores[1]	95,000
Reserves in zinc ores[2]	12,500
Resources in copper ores[3]	30,000
Reserves in copper ores[4]	6300
Total indium resources	125,000
Total indium reserves	18,800

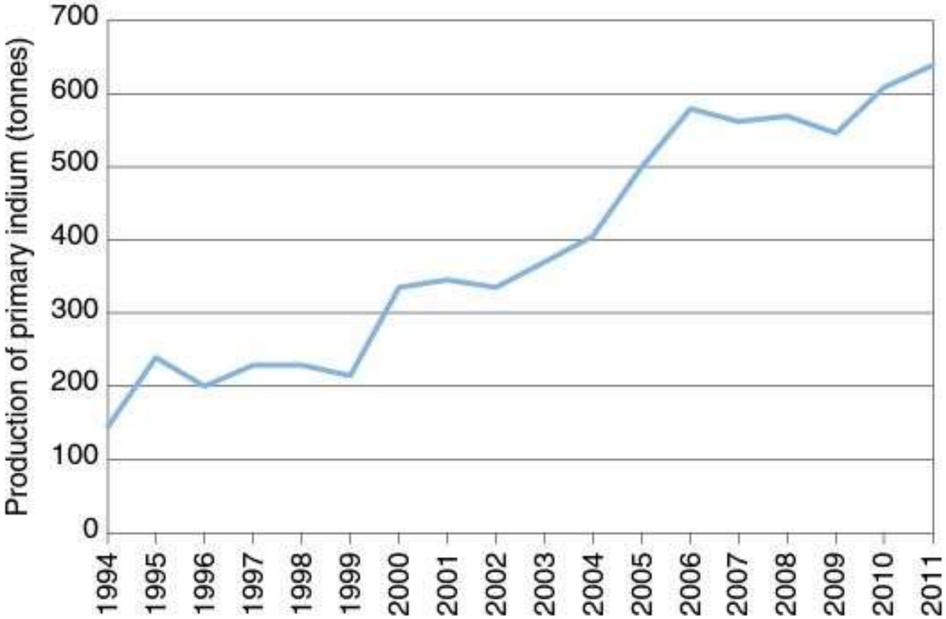
[1] calculated from global zinc resources with indium concentration of 50 g/t

[2] calculated from global zinc reserves with indium concentration of 50 g/t

[3] calculated from global copper resources with indium concentration of 10 g/t

[4] calculated from global copper reserves with indium concentration of 10 g/t

In – production



Global primary indium production, 1994–2011. (Data from USGS, 2012c.)

Table 9.6 Estimated indium mine production in 2009 from base metal zinc deposits. (Data from Roskill, 2010.)

	Zinc mine production	Mine production zinc concentrate	Estimated indium concentration and quantity in the concentrate		Share
Country	**(million tonnes contained zinc)**	**(million tonnes sphalerite)**	**(ppm)**	**(tonnes)**	**%**
Australia	1.3	1.9	15	29	6.2
Canada	0.7	1.1	37	40	8.6
China	2.8	4.2	50	210	45.0
Mexico	0.5	0.8	20	16	3.4
Peru	1.5	2.2	20	44	9.4
USA	0.7	1	20	21	4.5
Other countries	3.6	5.4	20	107	23.0
Total	11.1	16.6	29	467	100

In – producers and prices

Table 9.7 Important global indium producers. (Data from Roskill, 2010 and USGS, 2009.)

	Country	Refinery capacity (tonnes)	Secondary capacity (tonnes)
Nanjaing Germanium Factory	China	150	
Huludao Zinc	China	50	
Zhuzhou Smelter Group	China	?	
Dowa Metals & Mining Co	Japan	70	150
Asahi Pretec Corp	Japan		200
Mitsubishi Mat. Group	Japan		96
Korea Zinc	Rep. of Korea	100	
Umicore SA	Belgium	30	
Teck Resources Ltd	Canada	~75	
Xstrata plc	Canada	?	

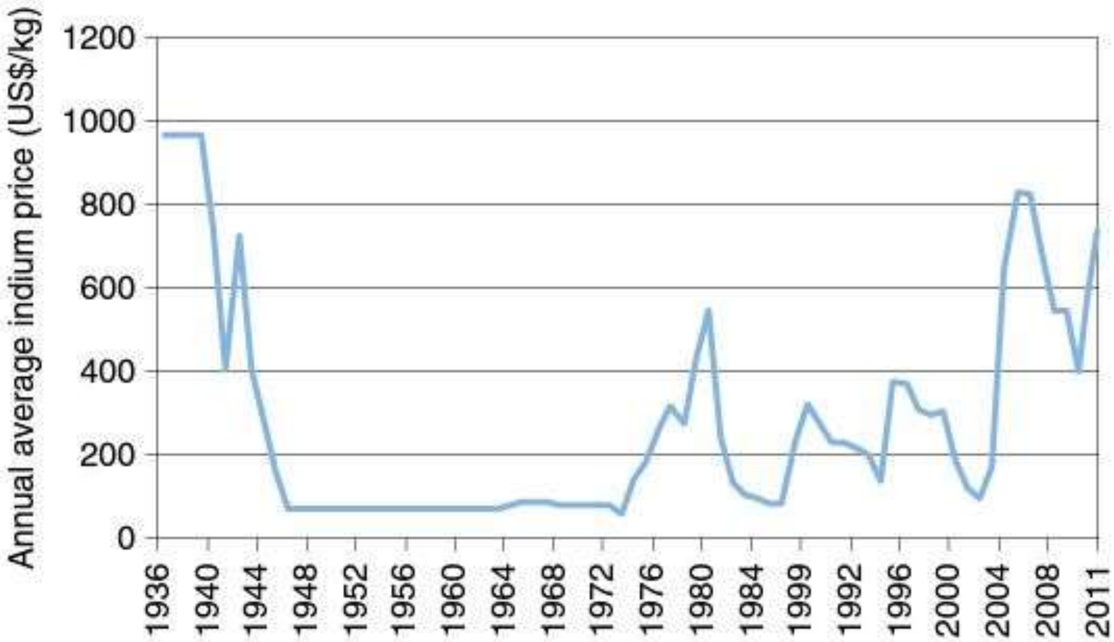


Figure 9.6 Annual average indium prices between 1936 and 2011. (Data from BGR database.)

In – environmental issues

- The environmental impacts of the mining and processing of **sulfide-rich In-bearing ores** are dependent on a wide range of factors: **ARD** (acid rock drainage); **tailing ponds** containing high abundances of Pb, Zn, Cd, Bi, Sb.

- Although the toxicity of In metal is low and harmful effects are not reported, some In compounds are toxic (**In phosphide is carcinogenic in animals**).

- **ITO** is the predominant form in which In is currently used: it can potentially cause a several type of **lung damage**, as well as **systemic toxicity** in mammals (kidneys, liver, blood, lungs, reproductive and developmental systems).

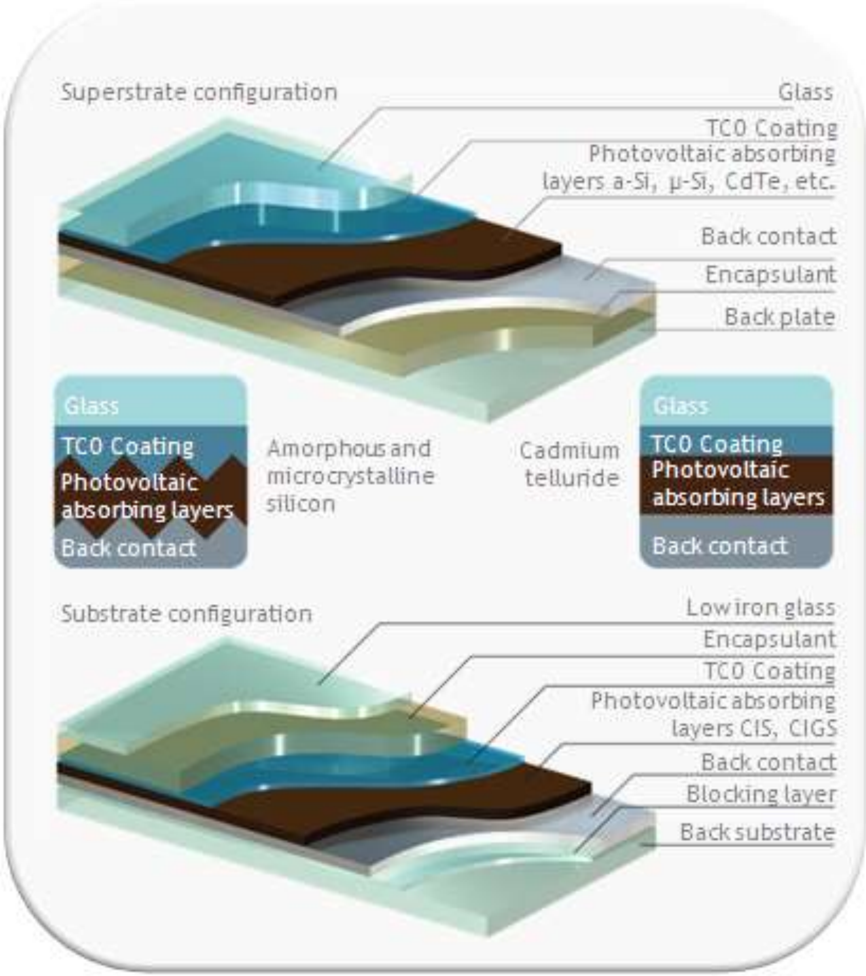
- Much remains unknown about In natural and anthropogenic cycling and toxicity!

In – outlook

- The outlook for the In market is healthy, with demand predicted to **grow at a rate of** 5 – 10% per annum.

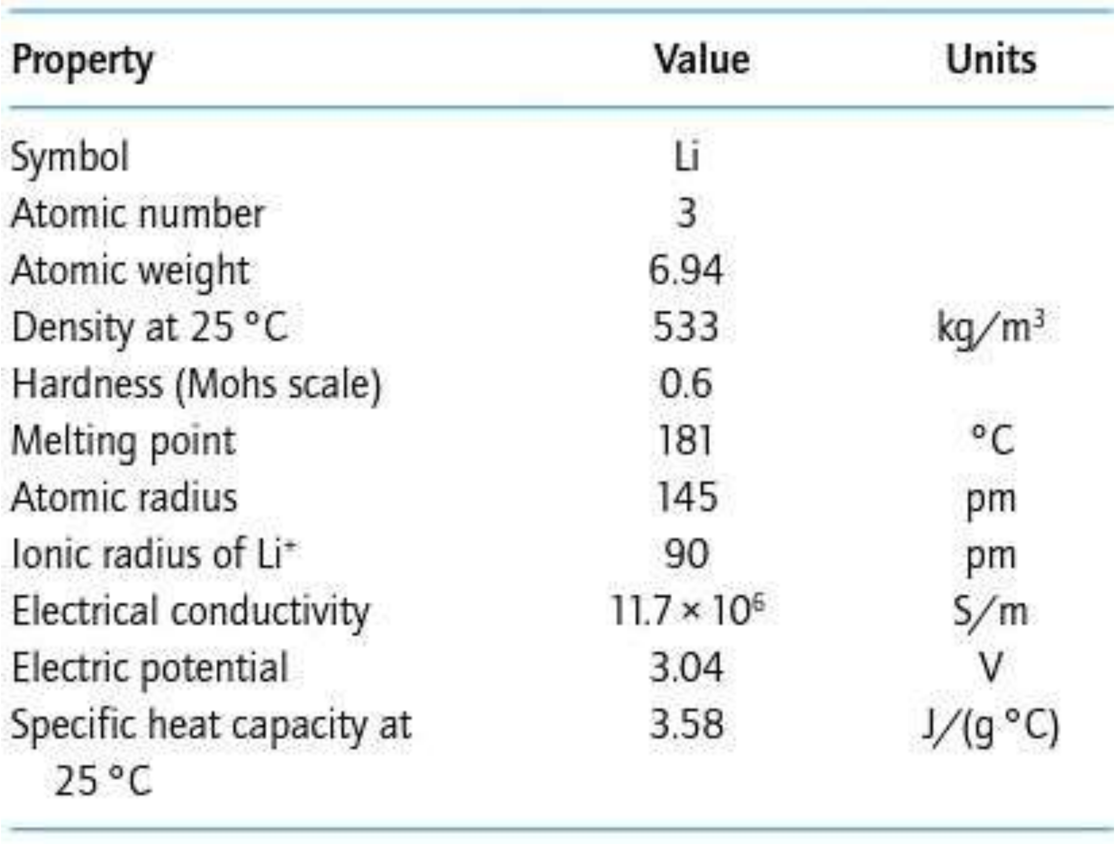
- Demand for **LCD panels** may increase more slowly, but it will continue as the main use of In.

- Another market area with significant potential to growth is in **thin-film photovoltaic cells** [In-Ga-selenide alloy (CIGS)].



Lithium

Li – definitions and characteristics



Property	Value	Units
Symbol	Li	
Atomic number	3	
Atomic weight	6.94	
Density at 25 °C	533	kg/m^3
Hardness (Mohs scale)	0.6	
Melting point	181	°C
Atomic radius	145	pm
Ionic radius of Li^+	90	pm
Electrical conductivity	11.7×10^6	S/m
Electric potential	3.04	V
Specific heat capacity at 25 °C	3.58	J/(g °C)

Li was discovered in **1817** by Johan Arfvedson, when he analyzed a sample of petalite. However, it was a year later when the pure metal was isolated.

Its name is derived from the Greek word "*lithos*", which means "stone".

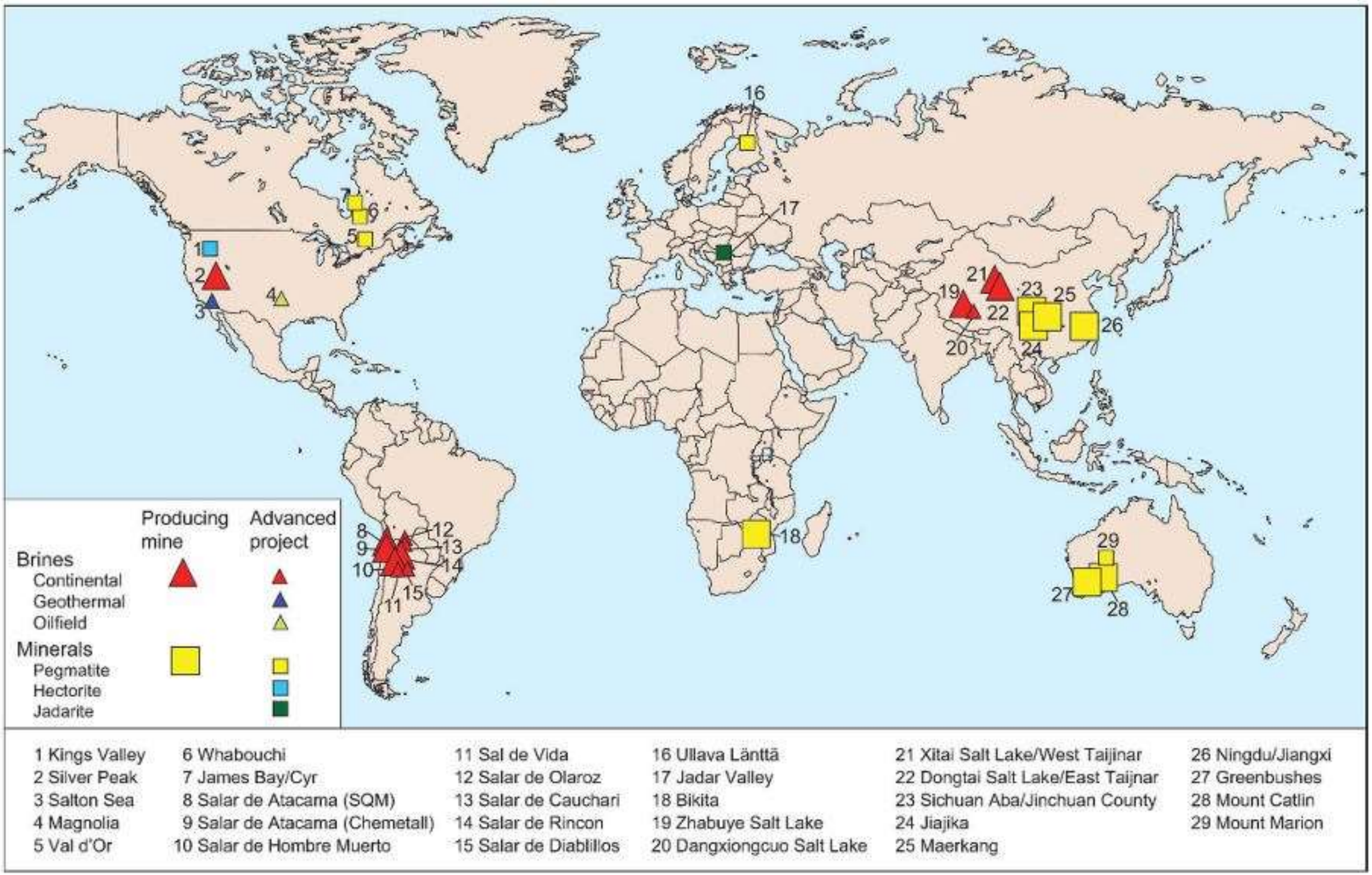
Due to its **high reactivity**, Li only occurs in nature in the form of compounds (silicates, clay minerals, chloride in brines).

Clarke: 17 ppm, ranging from 30 ppm (igneous rocks) to 60 ppm (sedimentary rocks). Seawater: 0.18 ppm.

- Concentration levels of Li in **pegmatites and ore concentrates** are reported as **percentage lithia (Li_2O)**.
- **Brine grades** are reported as **ppm**, mg per liter (**mg/l**) or weight % Li (**wt.% Li**).
- Because a great range of chemicals are produced, **production tonnages** are often expressed as **tons of Li carbonate equivalents (LCEs)**. Li carbonate contains 0.188 Li.

Li – mineralogy and deposit types

- Commercially viable concentrations of Li are found in **pegmatites**, **continental brines**, **geothermal brines**, **oilfield brines**, the clay mineral **hectorite** $Na_{0.33}(Mg, \mathbf{Li})_3Si_4O_{10}(F, OH)_2$ and the newly discovered **jadarite** $Na_2O\mathbf{Li}_2O(SiO_2)_2(B_2O_3)_3H_2O$.



Li – major deposit classes

- **PEGMATITES**: Li-containing pegmatites are relatively rare and frequently also contain Sn and tantalite. **Spodumene $LiAlSi_2O_6$** is the most common mineral (7.9% Li_2O). **Petalite $LiAlSi_4O_{10}$** is less common (4.2% Li_2O), and **lepidolite** (group name for trioctahedral Li-rich micas) is equally rare.

- **CONTINENTAL BRINES**: the term refers to brines in **enclosed (endorheic) basins** where inflowing surface and sub-surface waters contain modest quantities of Li which has been released from surrounding volcanic rocks as a result of **weathering**. Li becomes concentrated along with other elements of economic interest, particularly **K** and **B**, as a result of **high evaporation rates**.

- **GEOTHERMAL BRINES**: Li-containing geothermal brines are known at Wairakei in New Zealand (13 ppm), at the Reykanes Field in Iceland (8 ppm) and El Tatio in Chile (47 ppm).

- **OILFIELD BRINES**: the Smackover Formation (Texas, Arkansas, Oklahoma, Wyoming and North Dakota) contains brines grading up to 700 mg/l Li (also a major source of Br).

- **HECTORITE**: a clay mineral $Na_{0.33}(Mg, \mathbf{Li})_3Si_4O_{10}(F, OH)_2$ containing 0.53% Li. Western Lithium USA Inc. is developing the northern Nevada hectorite deposit.

- **JADARITE**: a newly discovered mineral $LiNaSiB_3O_7(OH)$ containing Li_2O 7.3%.

Li – Andean brines

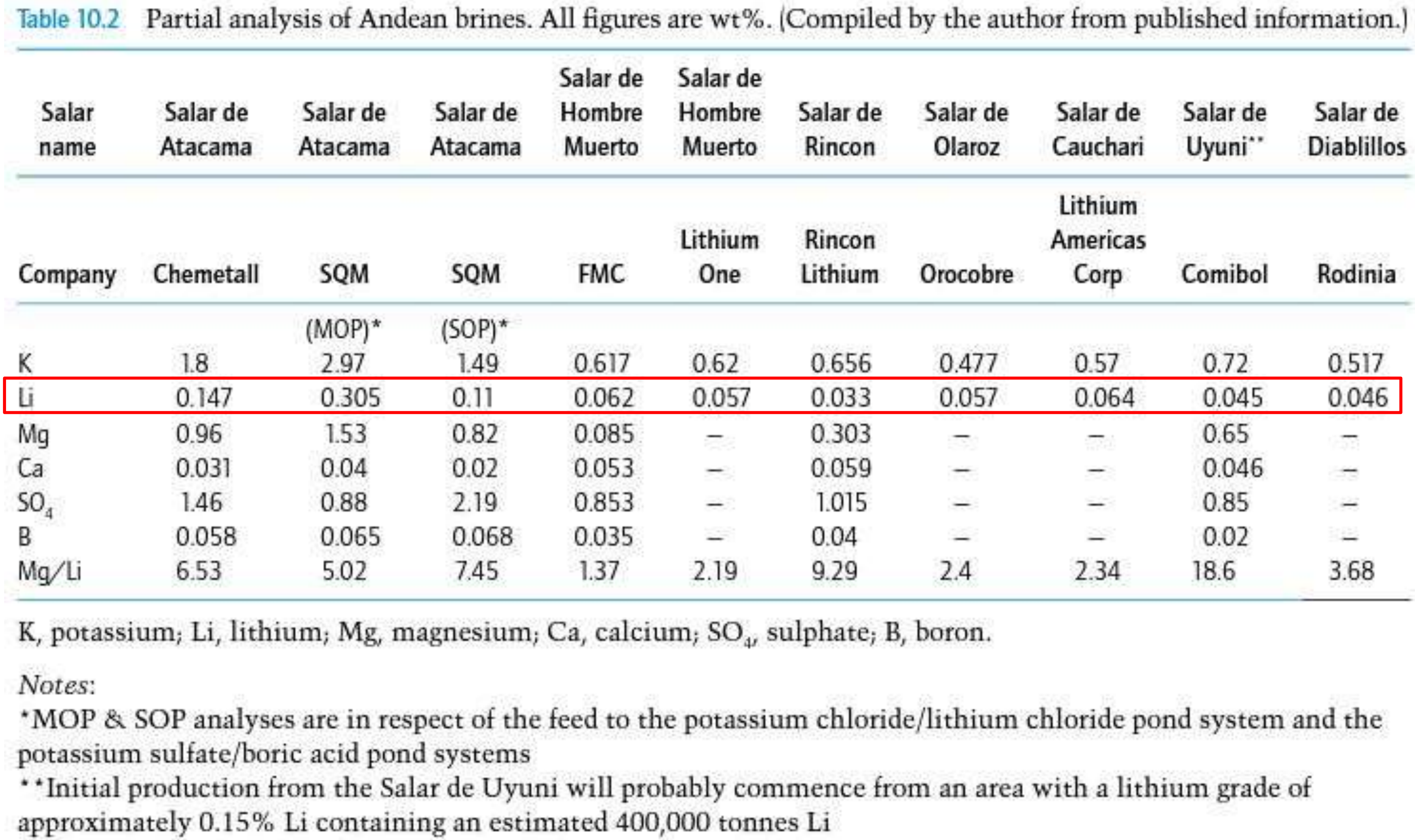


Table 10.2 Partial analysis of Andean brines. All figures are wt%. (Compiled by the author from published information.)

Salar name	Salar de Atacama	Salar de Atacama	Salar de Atacama	Salar de Hombre Muerto	Salar de Hombre Muerto	Salar de Rincon	Salar de Olaroz	Salar de Cauchari	Salar de Uyuni**	Salar de Diablillos
Company	Chemetall	SQM	SQM	FMC	Lithium One	Rincon Lithium	Orocobre	Lithium Americas Corp	Comibol	Rodinia
		(MOP)*	(SOP)*							
K	1.8	2.97	1.49	0.617	0.62	0.656	0.477	0.57	0.72	0.517
Li	0.147	0.305	0.11	0.062	0.057	0.033	0.057	0.064	0.045	0.046
Mg	0.96	1.53	0.82	0.085	–	0.303	–	–	0.65	–
Ca	0.031	0.04	0.02	0.053	–	0.059	–	–	0.046	–
SO_4	1.46	0.88	2.19	0.853	–	1.015	–	–	0.85	–
B	0.058	0.065	0.068	0.035	–	0.04	–	–	0.02	–
Mg/Li	6.53	5.02	7.45	1.37	2.19	9.29	2.4	2.34	18.6	3.68

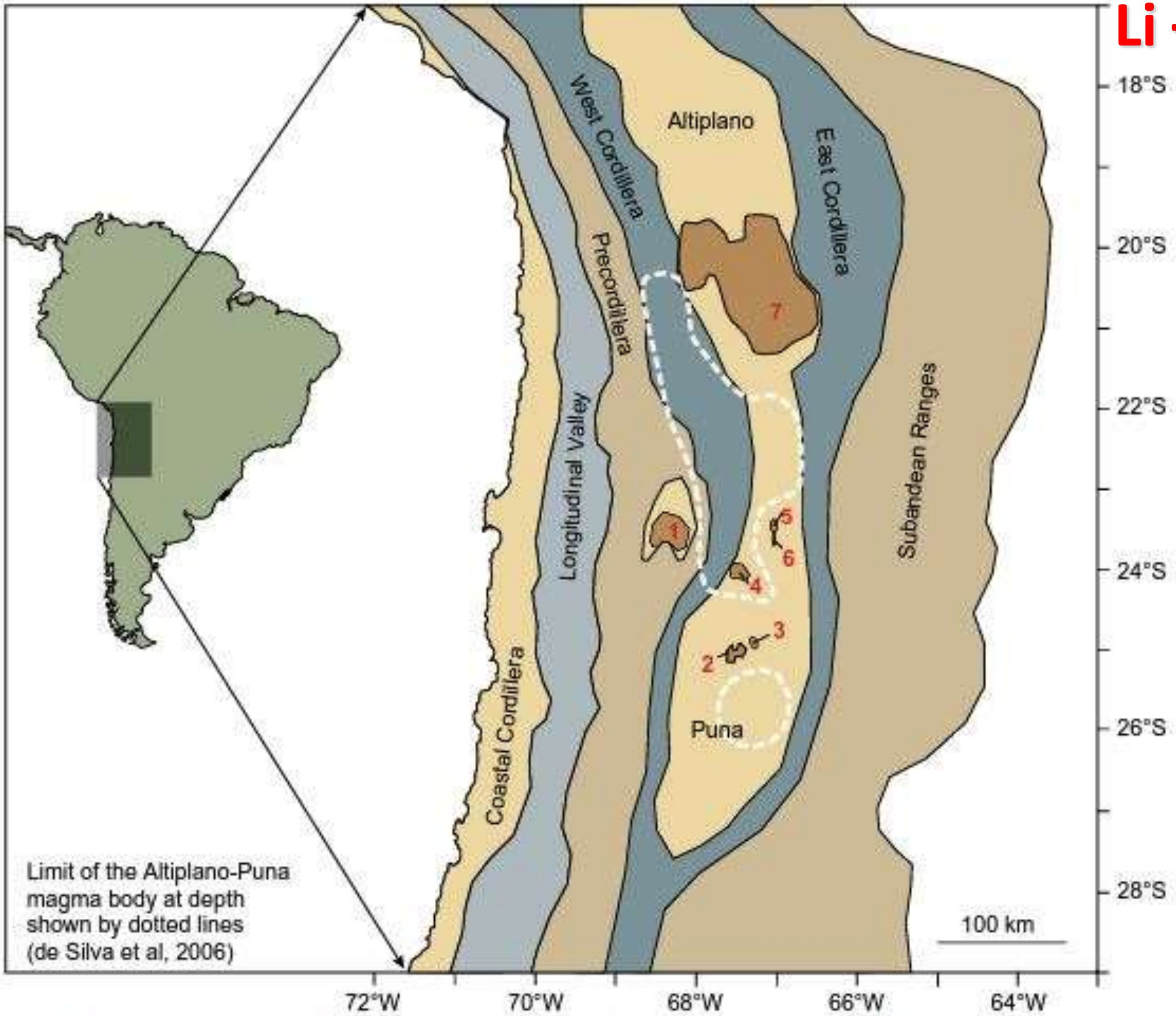
K, potassium; Li, lithium; Mg, magnesium; Ca, calcium; SO_4, sulphate; B, boron.

Notes:

*MOP & SOP analyses are in respect of the feed to the potassium chloride/lithium chloride pond system and the potassium sulfate/boric acid pond systems

**Initial production from the Salar de Uyuni will probably commence from an area with a lithium grade of approximately 0.15% Li containing an estimated 400,000 tonnes Li

Li – major deposit classes: salar



Limit of the Altiplano-Puna magma body at depth shown by dotted lines (de Silva et al, 2006)

1 Salar de Atacama   2 Salar de Hombre Muerto   3 Salar de Diablillos   4 Salar de Rincon
5 Salar de Olaroz   6 Salar de Cauchari   7 Salar de Uyuni

Figure 10.2 Location of salars in the Andean region where lithium extraction is active or proposed. (Compiled by John Houston.)

Li – major deposit classes: hectorite-rich clay lenses

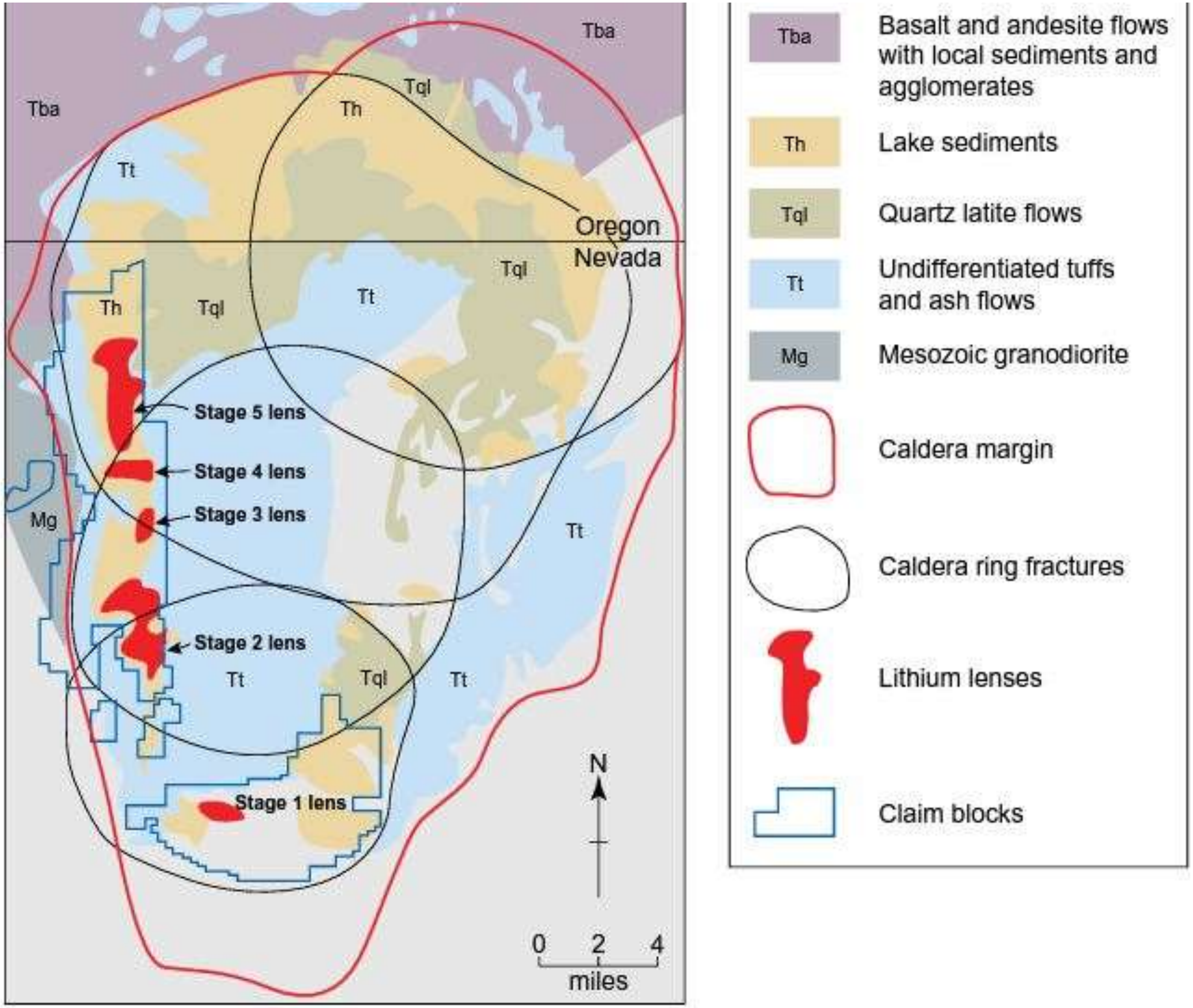


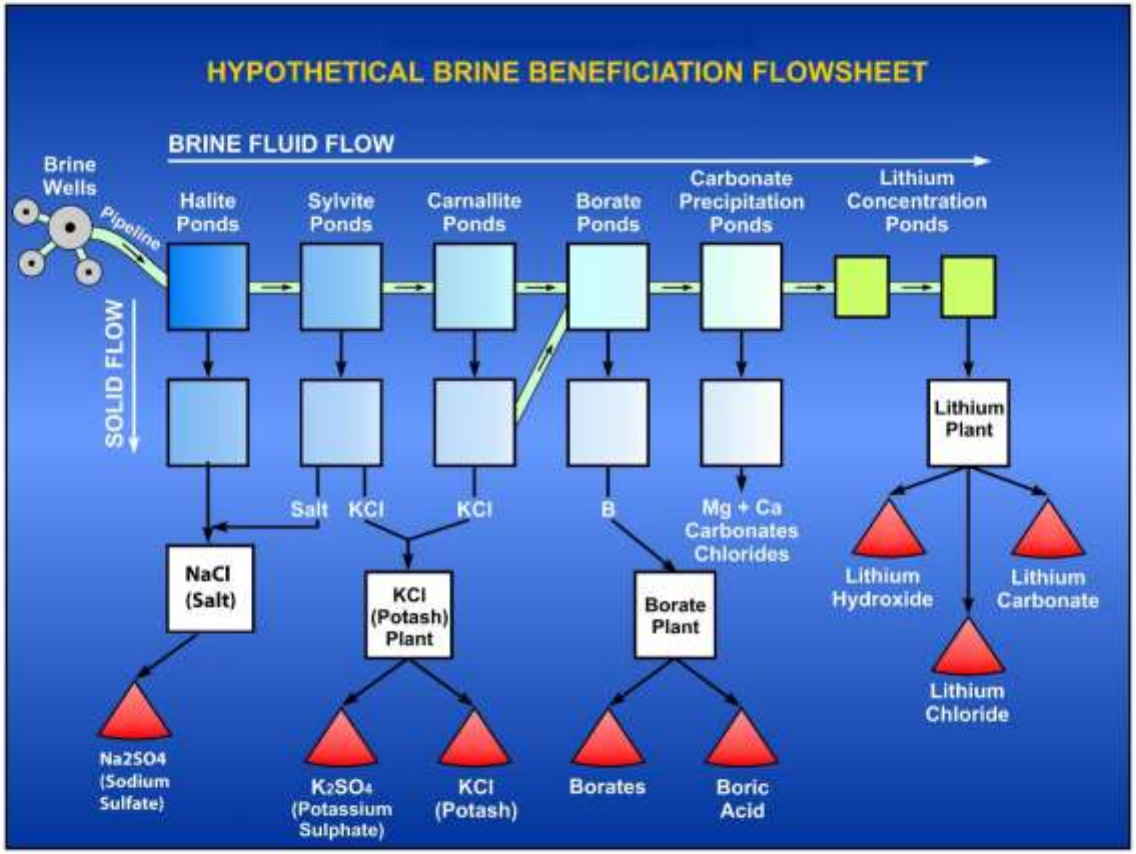
Figure 10.10 Geological map of Kings Valley showing the five hectorite-rich clay lenses. (Modified from Chmelauskas, 2010.)

Li – extraction methods and processing

- Currently Li is produced from **pegmatite** and **continental brine** sources. Most **spodumene**-based pipeline projects will use an acid leach process to produce **Li carbonate**.

- Methods of processing **continental brines** vary considerably depending on the overall chemistry. The basic aim is to concentrate the brines by **solar evaporation**: this involves the precipitation of unwanted elements such as NaCl, excess Ca, sulfate and Mg. Another process is ion-exchange (Hombre Muerto).

C3 Pit at the Greenbushes pegmatite in W. Australia, the world’s leading source of spodumene.



Li – specifications and uses

The market of Li is divisible into two major segments:

1. **Mineral concentrates** with **spodumene** with minor petalite and lepidolite;
2. Large range of **Li chemicals** and **metal**.

- **Non-chemical demand**: glasses, ceramics and glass-ceramics (lithia **reduces melting T** and provides **thermal shock resistance**).

- **Chemical demand**: > 200 Li-containing products are marketed.
  - **Li carbonate**: glass and ceramics, glass ceramics, enamel and glazes; Al electrolysis, cathodes for Li-ion batteries (mobile phones require 3 g Li carbonate for their batteries).
  - **Li hydroxide**: lubricating greases, CO_2 adsorbent (e.g. submarines and spacecraft).
  - **Li chloride**: used as a flux (Al), as a solution for controlling humidity.
  - **Li bromide**: large scale absorption-refrigeration systems.
  - **Li metal**: primary (non-rechargeable) battery anodes, organolithium compounds (butyllithium for synthetic rubber), Li-Al alloys (aircraft).

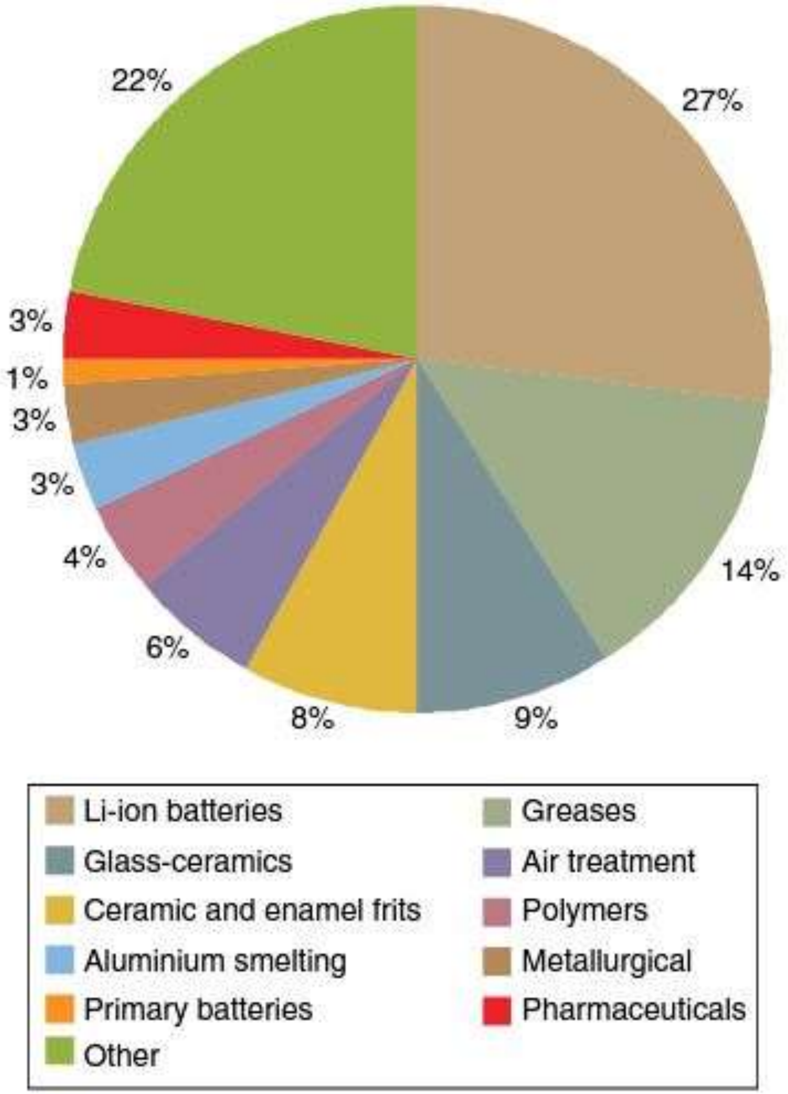
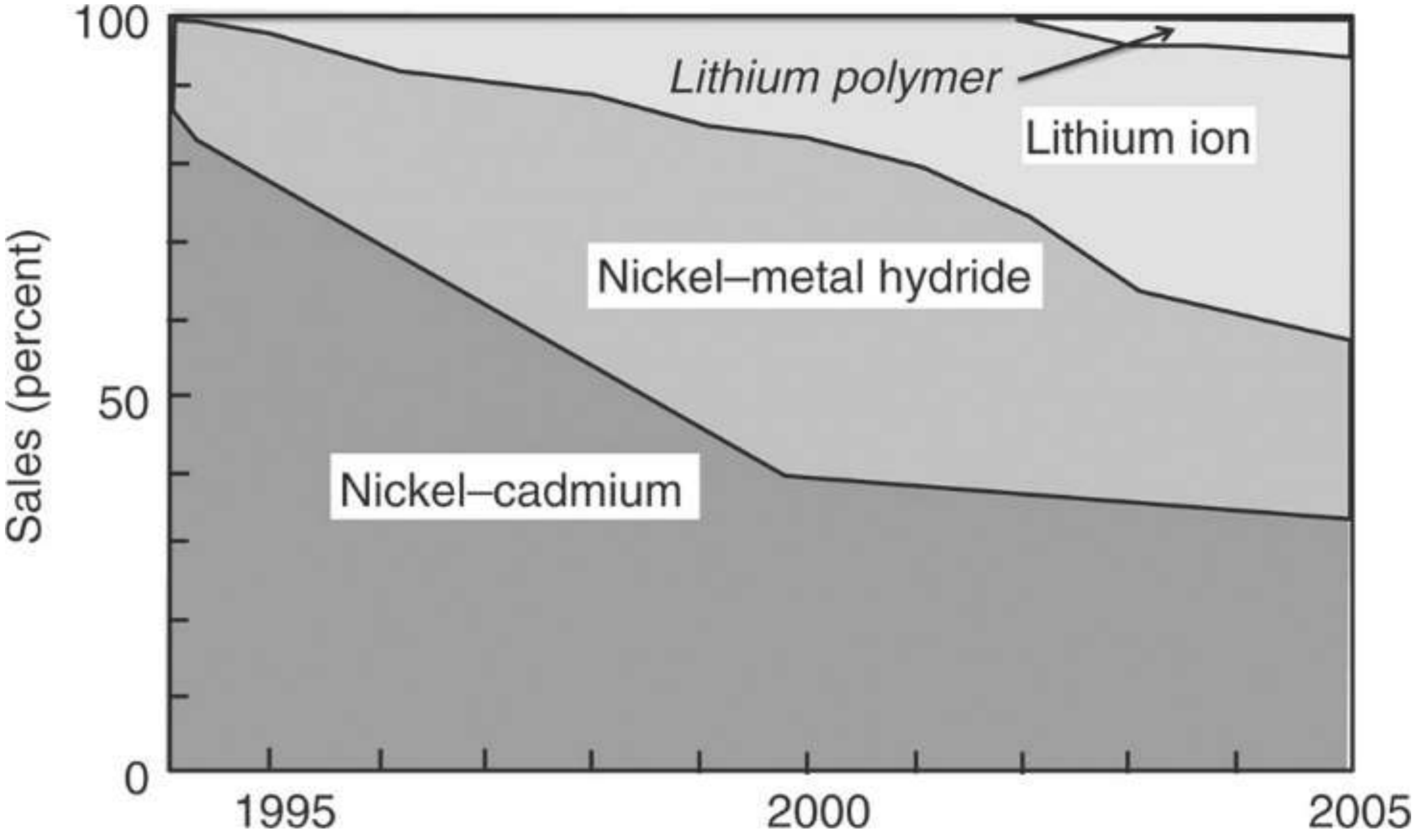


Figure 10.6 Lithium chemical uses, 2010. (Data from Roskill Information Services Ltd, personal communication.)

Li – metals in rechargeable batteries

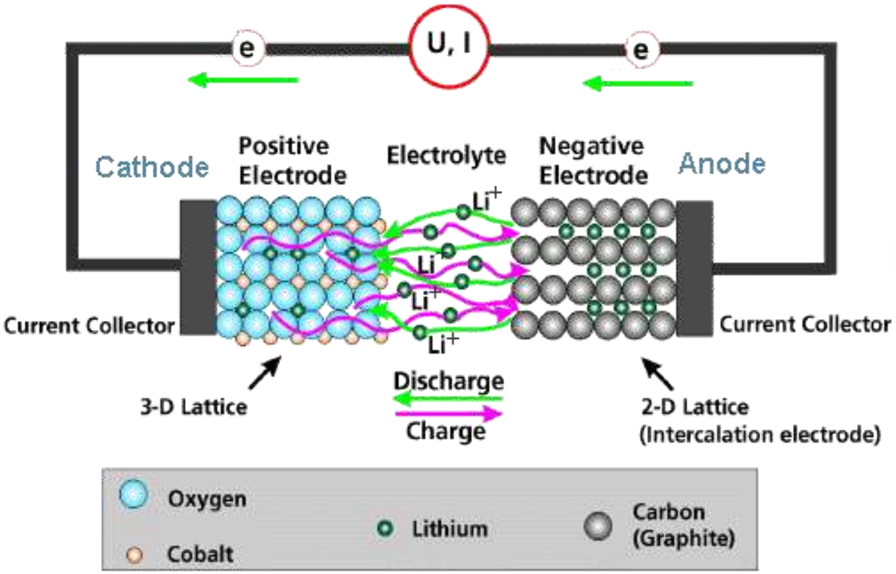


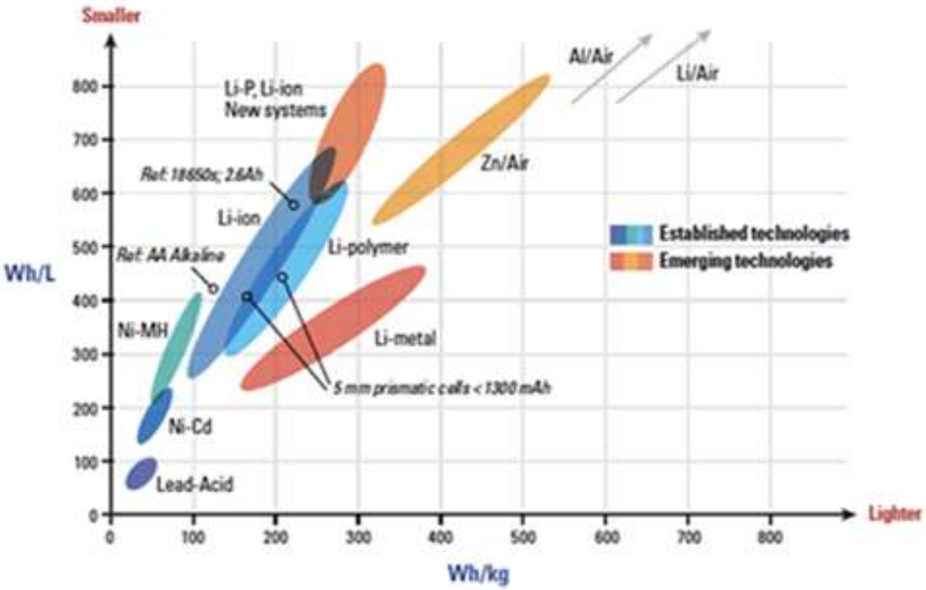
Li – recycling and substitution

- **Recycling**
  - **Electric vehicle (EV) batteries** differ significantly from existing batteries, and two recycling processes are applicable: **pyrometallurgical** and **hydrometallurgical**. The recycling chain for EV batteries is fairly complex.

- **Substitution**
  - **Primary batteries** (non-rechargeable): alkaline cells.

  - **Rechargeable batteries**: Pb acid, Ni-Cd, NiMH. There is no current competition for Li-ion in most electric vehicles.





Li – pegmatite resources

Table 10.3 Estimated world lithium resources compiled by the author based on previous work and published sources.

	Tonnes Li
Pegmatites	
North Carolina, USA *undeveloped	2,600,000
Manono, *D.R. Congo	2,300,000
Greenbushes, Australia (Talison)	1,500,000[‡]
Russia, numerous	1,000,000
China, numerous	750,000[‡]
Canada, others	430,000
North Carolina, USA (Former Operations)	230,000
Quebec Lithium, Canada (Canada Lithium)	230,000
Whabouchi, Canada (Nemaska)	187,000
Karalpa, Austria (E. Coast Minerals)	134,000
Lithium One, Canada (James Bay)	130,000
Mibra, Brazil (CIF Mineracao)	100,000
Mount Marion, Australia (Reed)	93,500
Mount Cattlin, Australia (Galaxy)	90,000[‡]
Brazil, other	85,000
Bikita, Zimbabwe	56,700[‡]
Lantiar, Finland (Keliber Oy)	14,000
Total Pegmatites	**9,930,000[‡]**

Li – continental brines & others

Continental Brines	
Salar de Uyuni, Bolivia (Comibol)	8,900,000
Salar de Atacama, Chile (SQM & Chemetall)	6,900,000[*]
China & Tibet, numerous	2,600,000[*]
Salar de Cauchari, Argentina (Lithium Americas)	1,520,000
Salar de Rincon, Argentina (Rincon Lithium)	1,400,000[*]
Salar de Olarez, Argentina (Orocobre)	1,200,000
Sal de Vida, Argentina (Lithium One)	1,020,000
Salar de Hombre Muerto, Argentina (FMC)	850,000[*]
Salar de Diablillos, Argentina (Rodinia)	530,000
Salar de Maricunga, Chile	200,000
Silver Peak, Nevada, USA (Chemetall)	40,000[*]
Total Continental Brines	**25,160,000**[*]
Others	
Hectorite	
Kings Valley, U.S.A (Western Lithium)	2,000,000
La Ventana, Sonora, Mexico (Bacanora)	180,000
Geothermal Brines	
Brawley, California (Simbol)	1,000,000
Jadarite	
Jadar, Serbia (Rio Tinto)	950,000
Oilfield Brines	
Smackover Formation, U.S.A (Albermarle)	850,000
Total Others	**4,980,000**
Total Overall	**40,070,000**

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*Adjusted for mining losses

Li – production

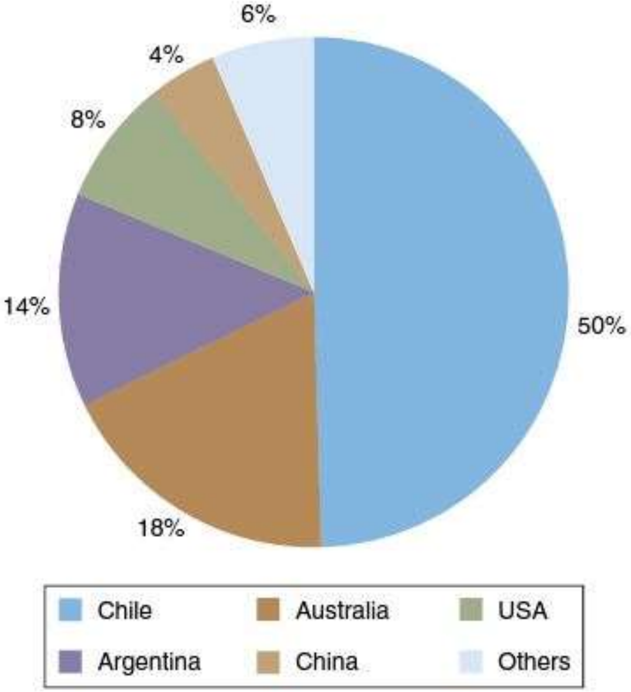
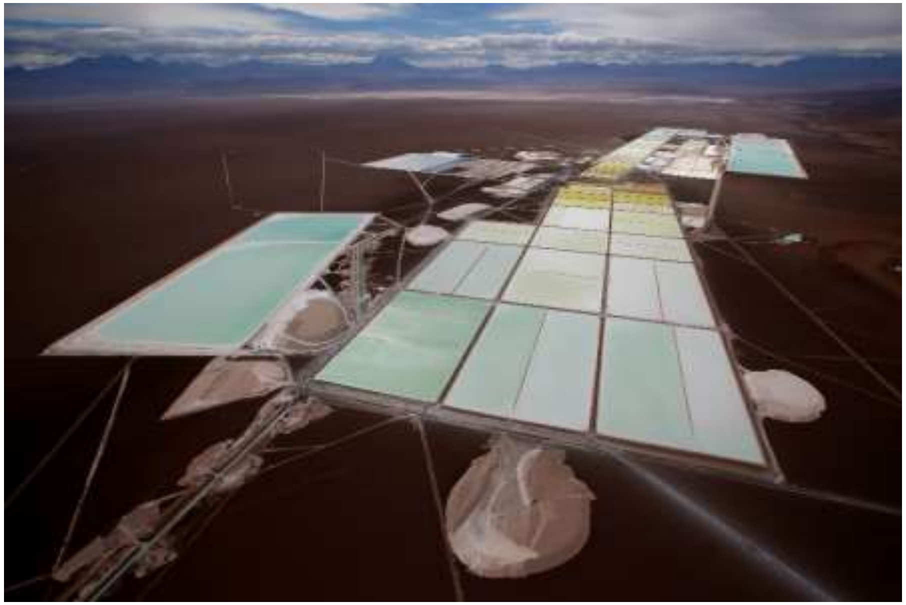
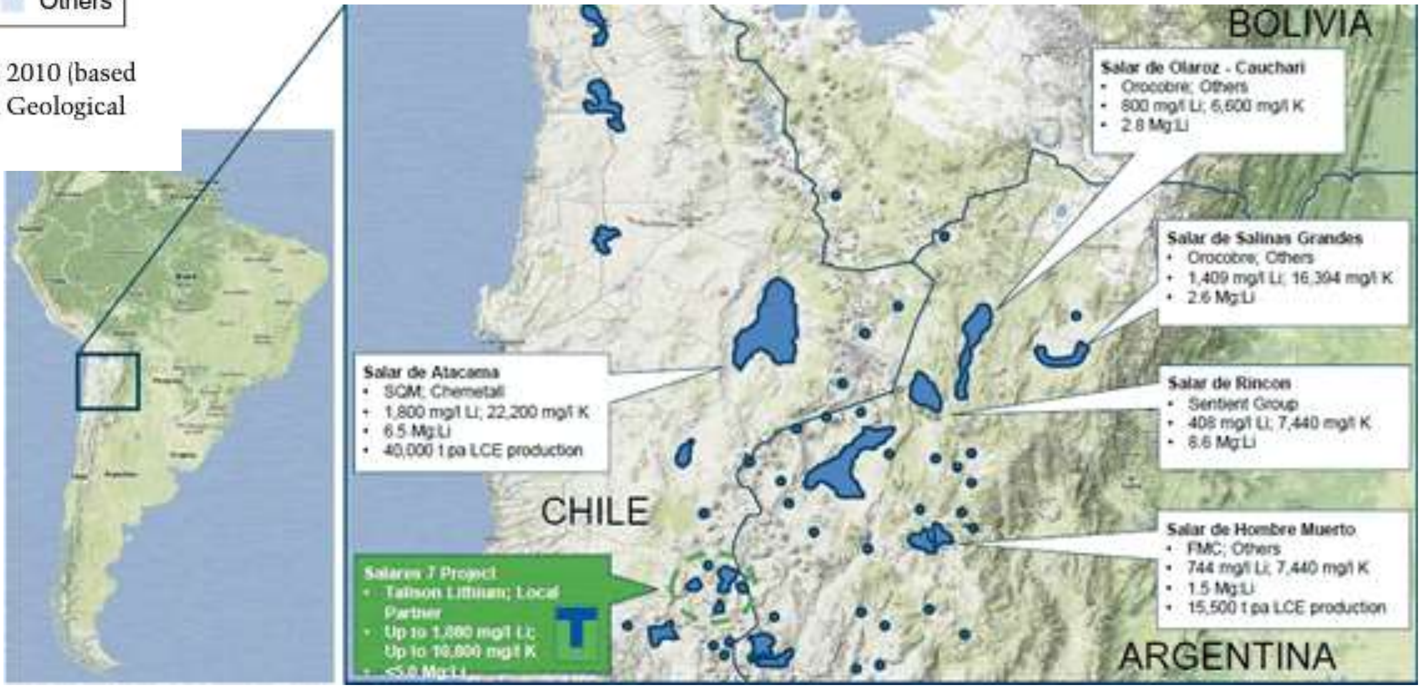


Figure 10.9 Lithium producing countries 2010 (based on tonnes Li content). (Data from British Geological Survey, 2012.)





Li – exporting countries

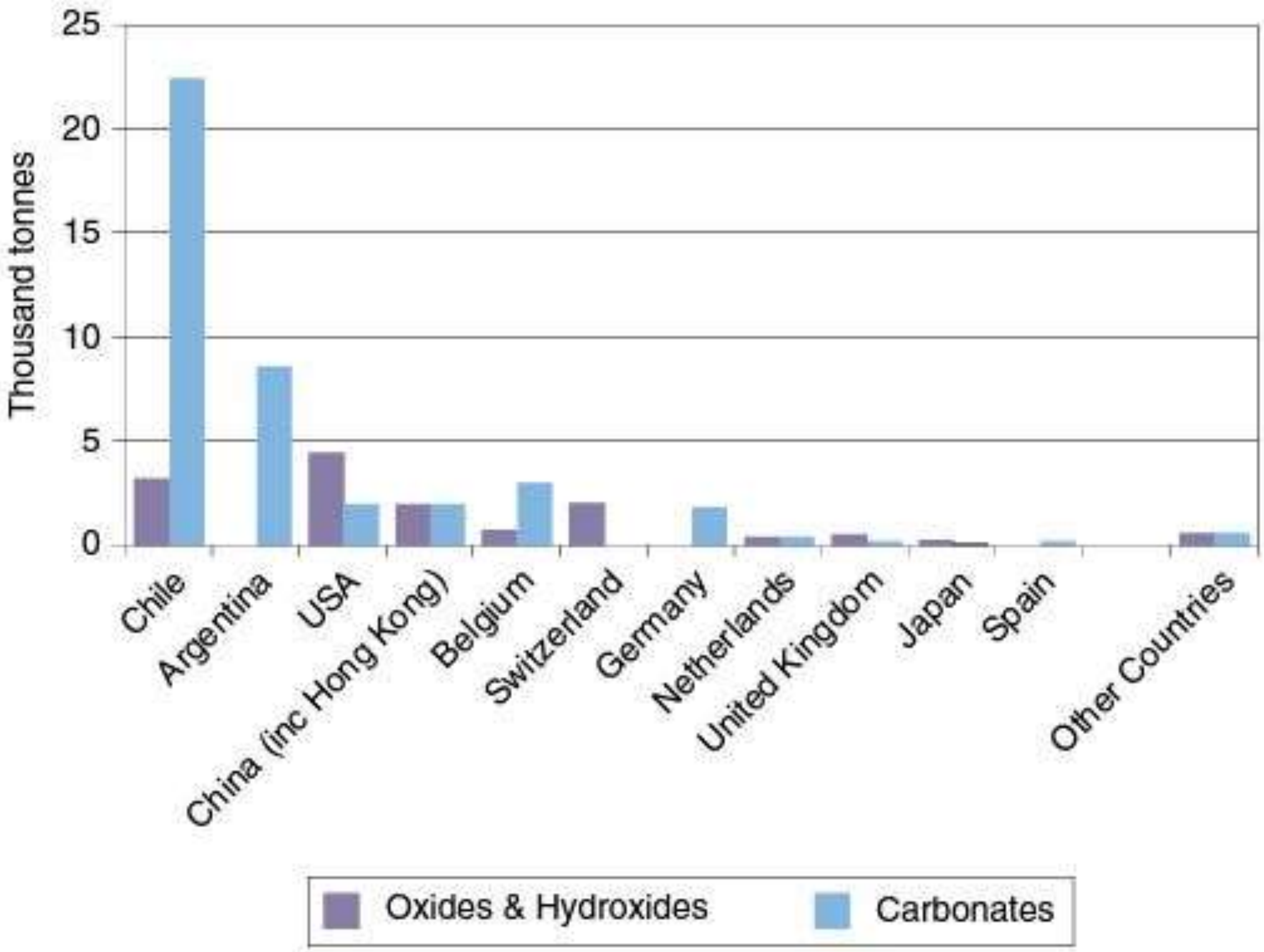


Figure 10.12 The main exporting countries for lithium carbonate, oxides and hydroxides, 2009. (Data from British Geological Survey World Mineral Statistics database and UN Comtrade, 2013.)

Li – importing countries

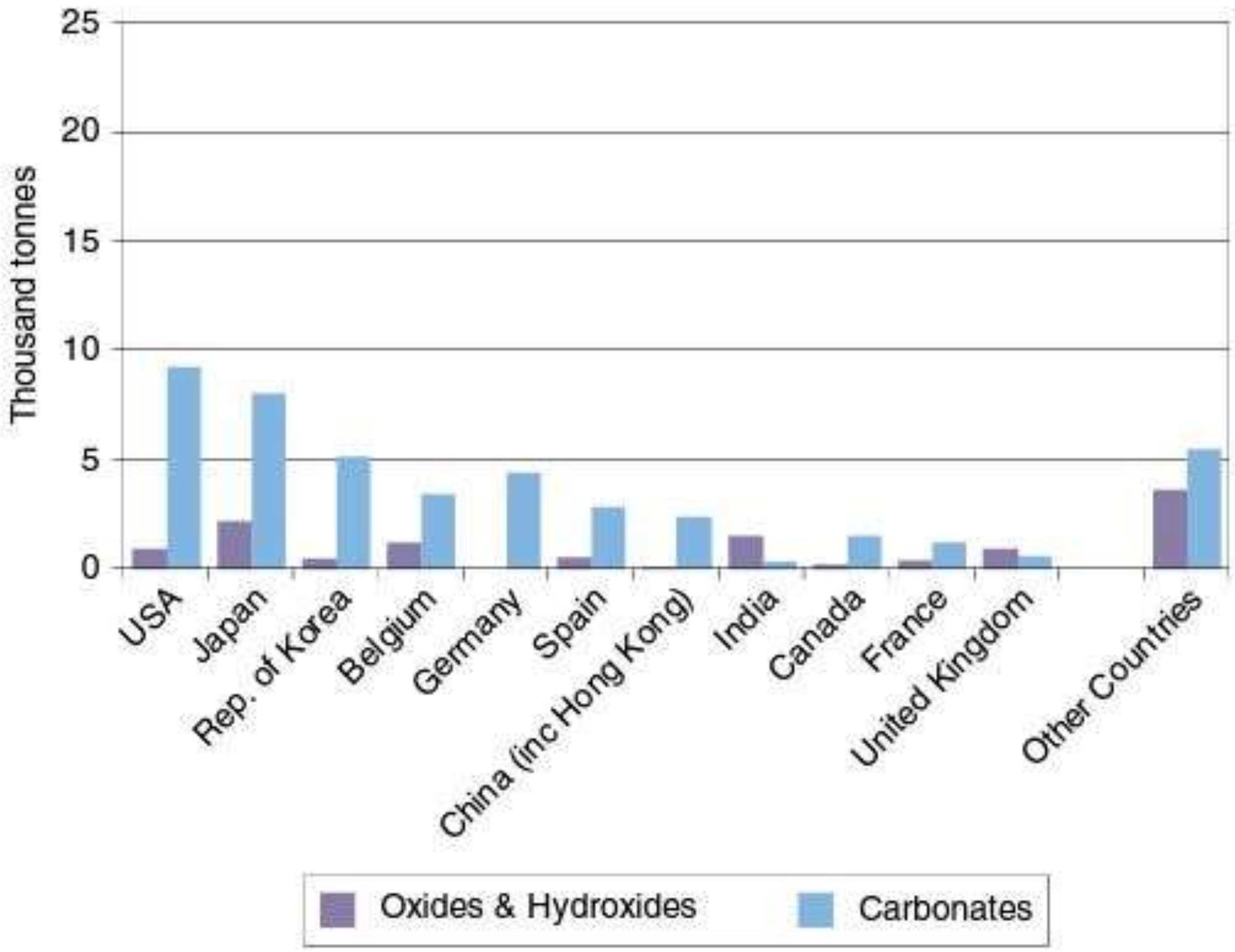
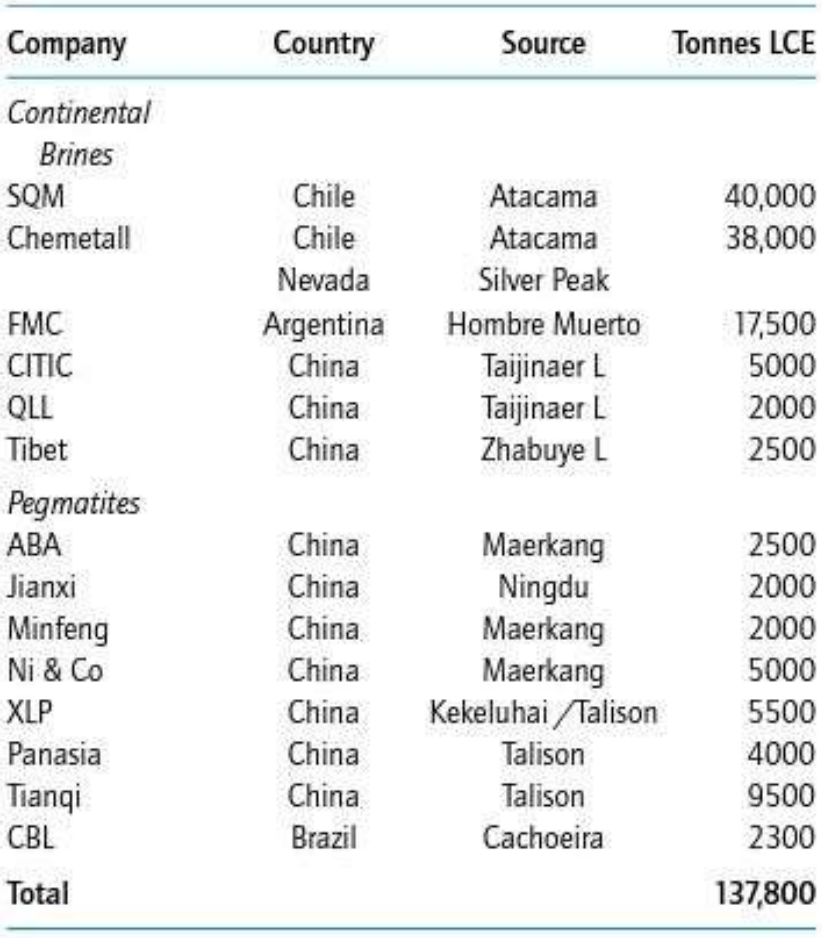


Figure 10.11 The main importing countries for lithium carbonate, oxides and hydroxides, 2009. (Data from British Geological Survey World Mineral Statistics database and UN Comtrade, 2013.)

Li – production

Table 10.4 Lithium chemical production capacities in 2010. (Data from Solminihac, 2010.)



Company	Country	Source	Tonnes LCE
Continental Brines			
SQM	Chile	Atacama	40,000
Chemetall	Chile	Atacama	38,000
	Nevada	Silver Peak	
FMC	Argentina	Hombre Muerto	17,500
CITIC	China	Taijinaer L	5000
QLL	China	Taijinaer L	2000
Tibet	China	Zhabuye L	2500
Pegmatites			
ABA	China	Maerkang	2500
Jianxi	China	Ningdu	2000
Minfeng	China	Maerkang	2000
Ni & Co	China	Maerkang	5000
XLP	China	Kekeluhai / Talison	5500
Panasia	China	Talison	4000
Tianqi	China	Talison	9500
CBL	Brazil	Cachoeira	2300
Total			**137,800**

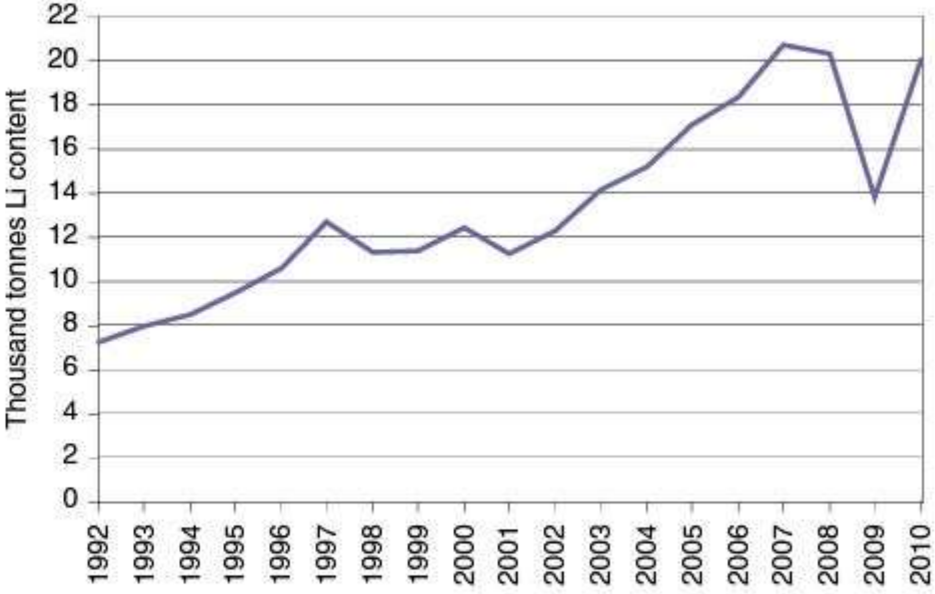


Figure 10.8 Worldwide annual production of lithium 1996–2010 (Li content). (Data from World Mineral Statistics Database, British Geological Survey.)

Li – environmental issues

- In **conventional brine-based projects**, the predominant waste product is **NaCl**.

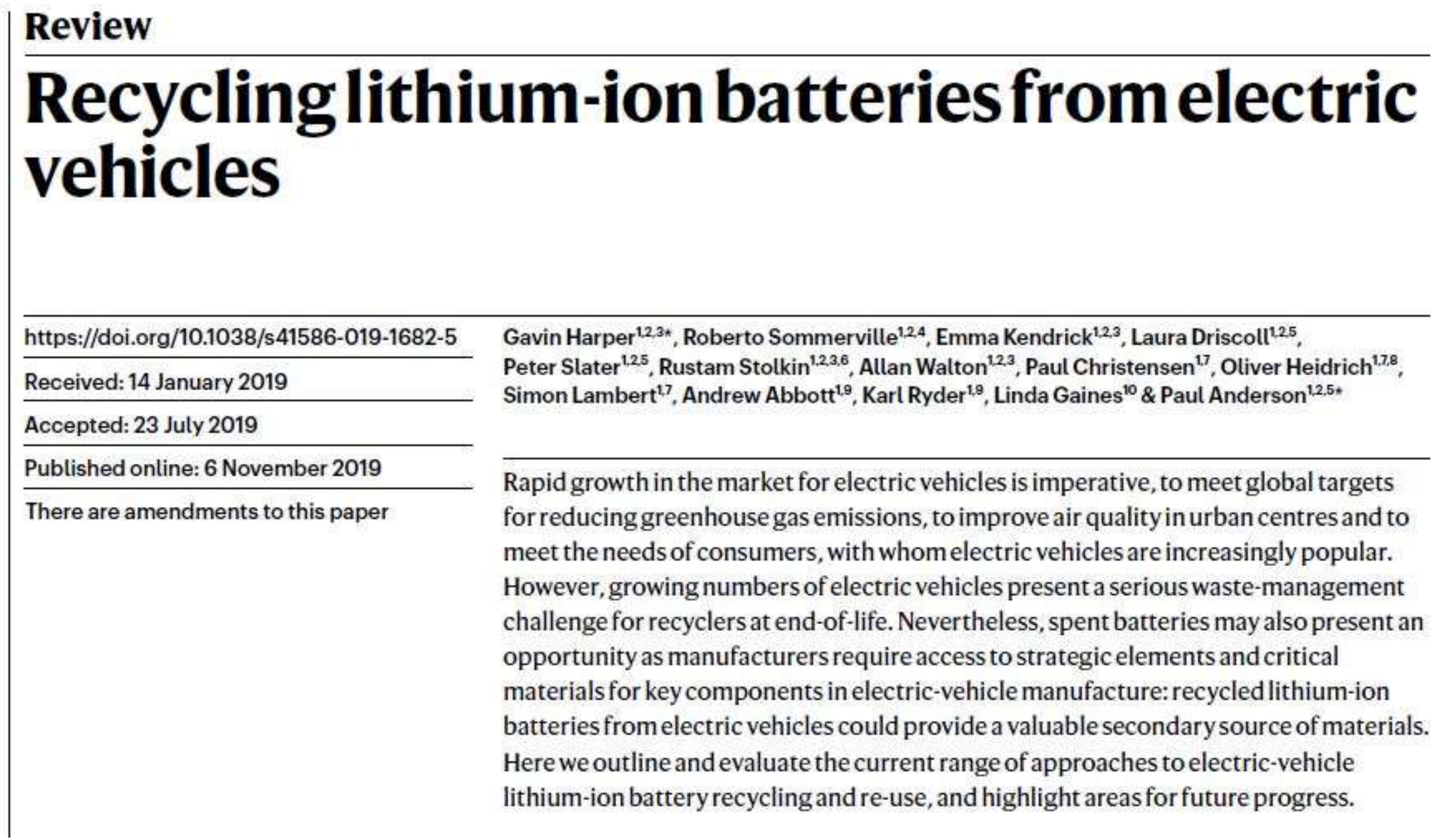
- Any **pegmatite** development will require similar permits as with any new mining operation and when onward processing from concentrate to carbonate is proposed the operation of a **kiln** will have an impact on air quality.

- **Used batteries** containing Li in cell phones and computers should be collected along with other electronic waste.

- In **glasses, glass ceramics** and **ceramics**, the Li is entrained in the products from which it cannot be leached after disposal.

- Li products are used in the synthesis of many **drugs** (manic depression), as a **sanitizer** in food-manufacturing facilities, laundries, swimming pools and hospitals. It presents few environmental problems in these applications.

Li – recycling



Review

Recycling lithium-ion batteries from electric vehicles

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There are amendments to this paper

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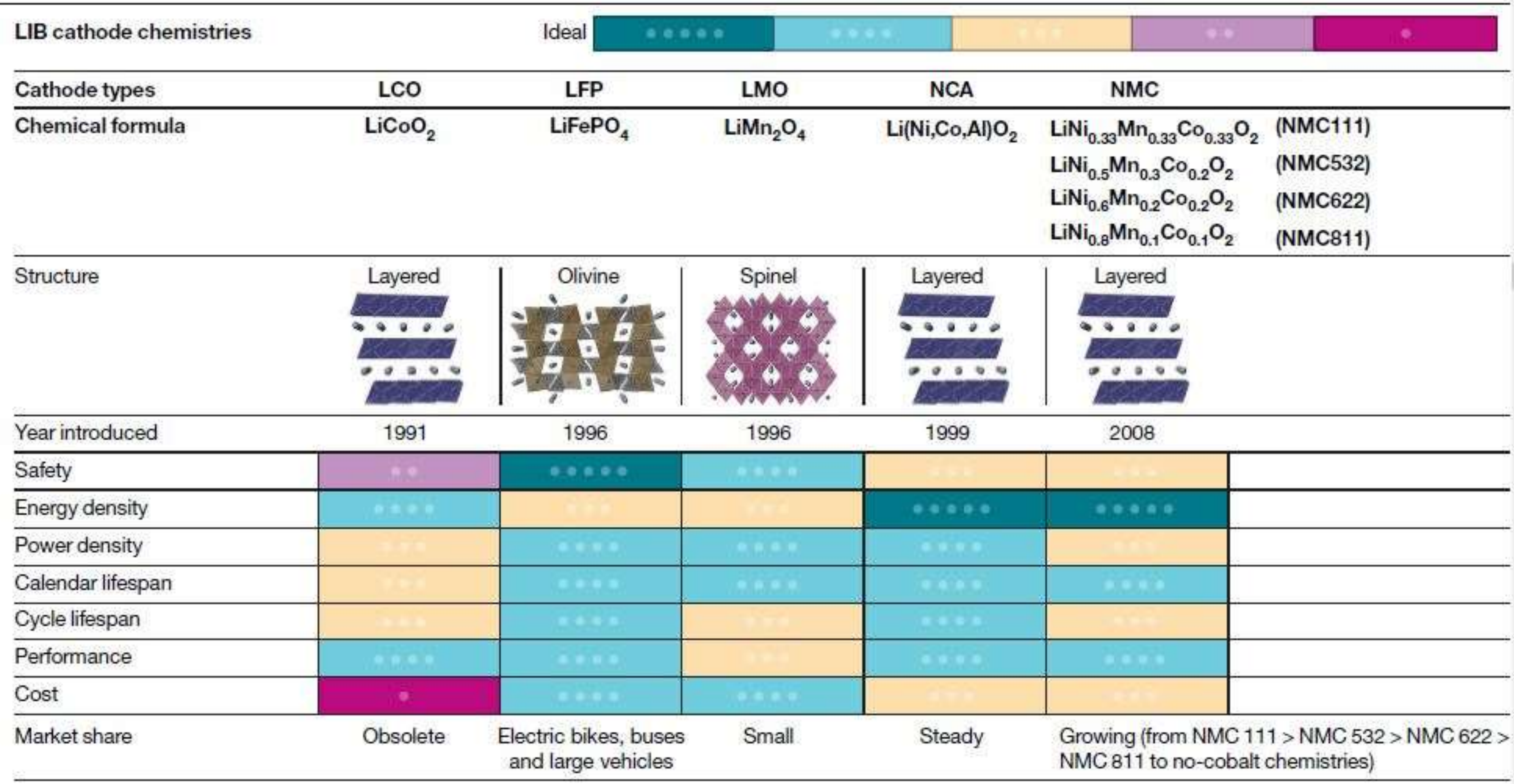
Rapid growth in the market for electric vehicles is imperative, to meet global targets for reducing greenhouse gas emissions, to improve air quality in urban centres and to meet the needs of consumers, with whom electric vehicles are increasingly popular. However, growing numbers of electric vehicles present a serious waste-management challenge for recyclers at end-of-life. Nevertheless, spent batteries may also present an opportunity as manufacturers require access to strategic elements and critical materials for key components in electric-vehicle manufacture: recycled lithium-ion batteries from electric vehicles could provide a valuable secondary source of materials. Here we outline and evaluate the current range of approaches to electric-vehicle lithium-ion battery recycling and re-use, and highlight areas for future progress.

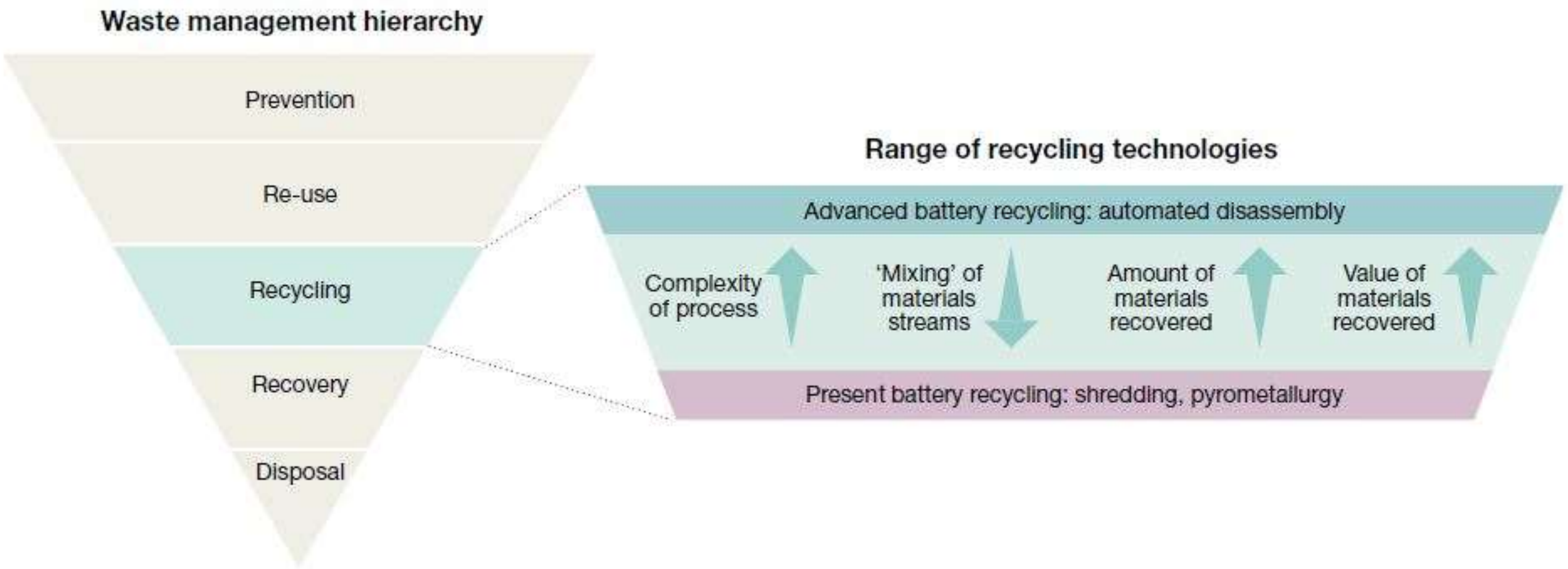
Li batteries – cathode type



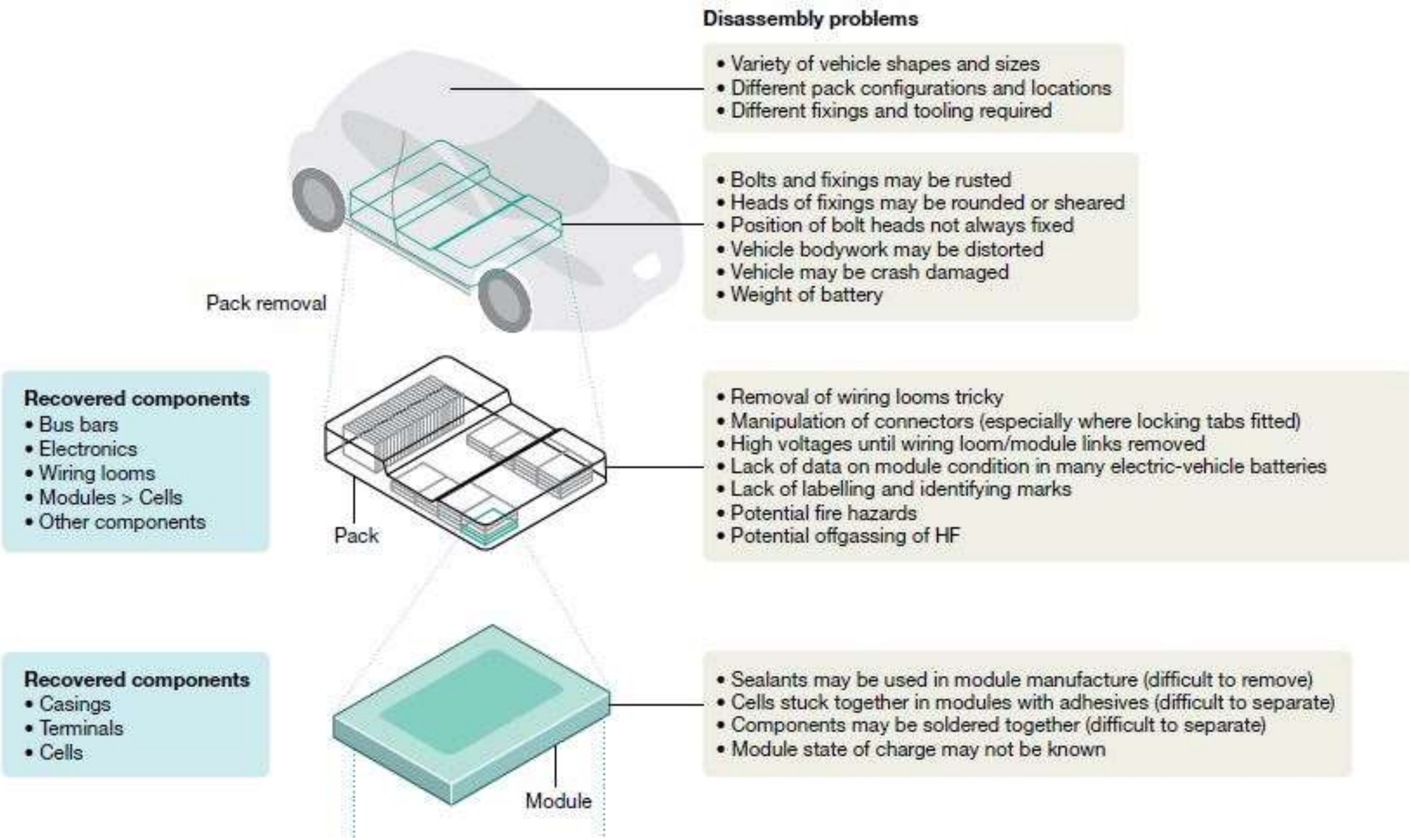
LIB cathode chemistries Ideal ●●●●● ●●●● ●●● ●● ●

Cathode types	**LCO**	**LFP**	**LMO**	**NCA**	**NMC**
Chemical formula	$LiCoO_2$	$LiFePO_4$	$LiMn_2O_4$	$Li(Ni,Co,Al)O_2$	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC111) $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811)
Structure	Layered	Olivine	Spinel	Layered	Layered
Year introduced	1991	1996	1996	1999	2008
Safety	●●	●●●●●	●●●●	●●●	●●●
Energy density	●●●●	●●●	●●●	●●●●●	●●●●●
Power density	●●●	●●●●	●●●●	●●●●	●●●
Calendar lifespan	●●●	●●●●	●●●●	●●●●	●●●●
Cycle lifespan	●●●	●●●●	●●●	●●●●	●●●
Performance	●●●●	●●●●	●●●	●●●●	●●●●
Cost	●	●●●●	●●●●	●●●	●●●
Market share	Obsolete	Electric bikes, buses and large vehicles	Small	Steady	Growing (from NMC 111 > NMC 532 > NMC 622 > NMC 811 to no-cobalt chemistries)

Li – recycling



Li – recycling: disassembly problems



Disassembly problems

- Variety of vehicle shapes and sizes
- Different pack configurations and locations
- Different fixings and tooling required

- Bolts and fixings may be rusted
- Heads of fixings may be rounded or sheared
- Position of bolt heads not always fixed
- Vehicle bodywork may be distorted
- Vehicle may be crash damaged
- Weight of battery

Recovered components

- Bus bars
- Electronics
- Wiring looms
- Modules > Cells
- Other components

- Removal of wiring looms tricky
- Manipulation of connectors (especially where locking tabs fitted)
- High voltages until wiring loom/module links removed
- Lack of data on module condition in many electric-vehicle batteries
- Lack of labelling and identifying marks
- Potential fire hazards
- Potential offgassing of HF

Recovered components

- Casings
- Terminals
- Cells

- Sealants may be used in module manufacture (difficult to remove)
- Cells stuck together in modules with adhesives (difficult to separate)
- Components may be soldered together (difficult to separate)
- Module state of charge may not be known

Li – recycling

Comparison of different LiB recycling methods

Best ●●●●● ●●●● ●●● ●● ● Worst

	Technology readiness	Complexity	Quality of recovered material	Quantity of recovered material	Waste generation	Energy usage	Capital cost	Production cost
Pyrometallurgy	●●●●●	●●●●●	●	●●●	●●	●	●	●●●●●
Hydrometallurgy	●●●●	●●●	●●●	●●●●	●●●	●●●	●●●	●●●
Direct recycling	●●	●	●●	●●●●●	●●●●	●●●	●●●	●

	Presorting of batteries required	Cathode morphology preserved	Material suitable for direct re-use	Cobalt recovered	Nickel recovered	Copper recovered	Manganese recovered	Aluminium recovered	Lithium recovered
Pyrometallurgy	●●●●●	No	No	●●●●●	●●●●●	●●●●●	●●●	No	●
Hydrometallurgy	●●●●	No	No	●●●●●	●●●●●	●●●●	●●●	●●●●●	●●●
Direct recycling	●	●●●●●	●●●●	●●●●●	●●●●●	●●●●●	●●●●●	●●●●●	●●●●●

Li – outlook

Estimating future Li demand is complicated by the extreme difficulty in estimating future battery demand for **hybrid vehicles** (HEVs), **plug-in hybrids** (PHEVs) or **pure electric** (EVs).

The requirement for the production of **fusion energy** is not included in any demand projections (any generating system will almost certainly employ a deuterium-tritium (DT) reaction, with the tritium obtained from Lithium's ^{6}Li isotope.

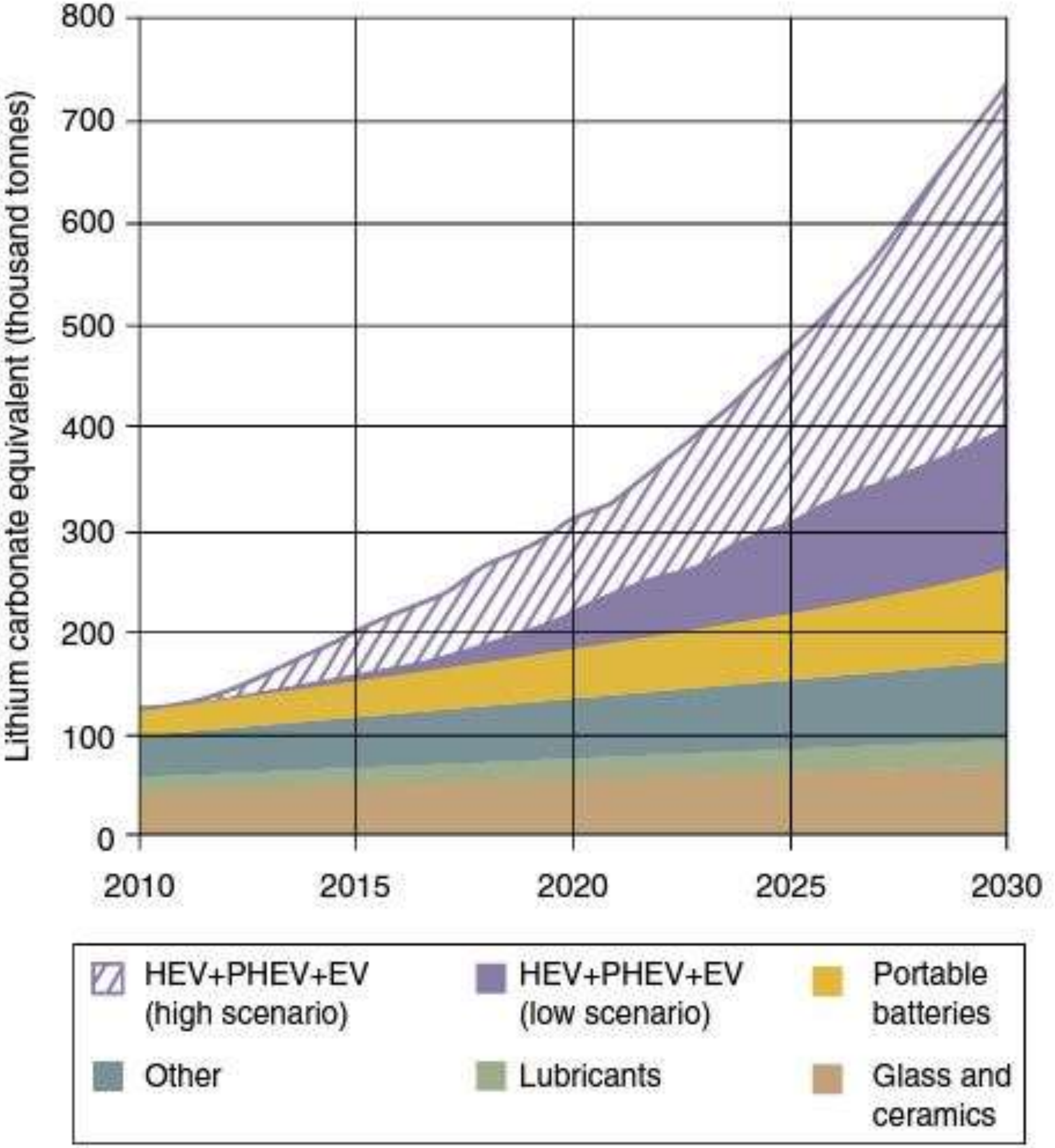
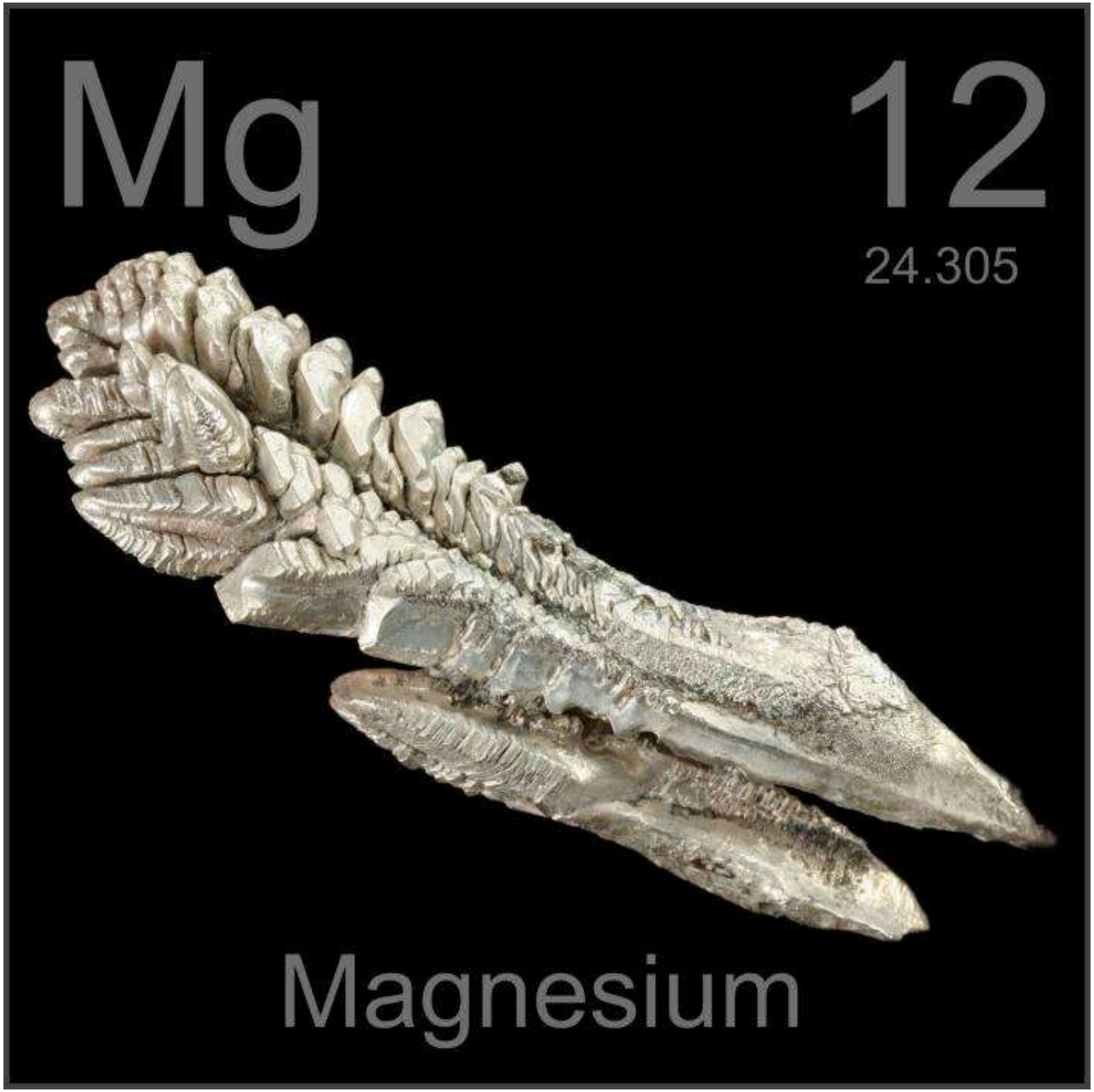


Figure 10.13 Forecast of the demand for lithium to 2030, with two different scenarios relating to the uptake of electric vehicles. (Courtesy of Rockwood Lithium.)

[redacted]

Magnesium



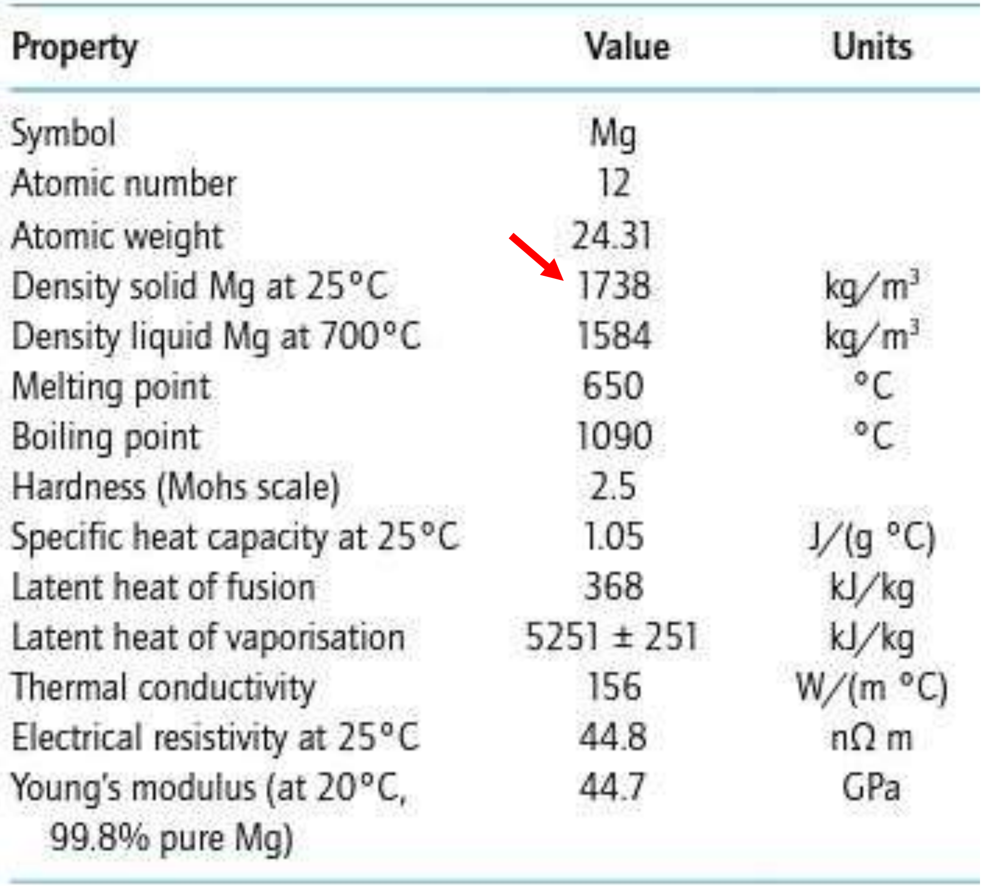
Mg – definitions and characteristics

On account of its **high strength** (150 – 400 MPa tensile strength) and **light weight**, Mg is the most commonly used **structural metal** after steel and Al.

About half of the Mg used today is in the production of **alloys**, most commonly with **Al**, with important applications in the **food industry** and in the **aerospace** and **military** sector. Mg, in its **structural applications**, is typically used as an **alloy casting** or as a **wrought alloy**. Typical mechanical properties: tensile strength 150 – 400 MPa, where cast alloys have lower tensile strength (e.g. portable electronic devices).

Mg metal is also unique in that it can be used as the **reducing agent** in the production of several special metals, such as **Be**, **Zr**, **U** and **Ti**.

Mg is the only structural metal that can be obtained from both the **lithosphere** and **hydrosphere**: Mg can be produced from **oxide resources** or from **chloride raw materials** originating from saline water.



Property	Value	Units
Symbol	Mg	
Atomic number	12	
Atomic weight	24.31	
Density solid Mg at 25°C	1738	kg/m^3
Density liquid Mg at 700°C	1584	kg/m^3
Melting point	650	°C
Boiling point	1090	°C
Hardness (Mohs scale)	2.5	
Specific heat capacity at 25°C	1.05	J/(g °C)
Latent heat of fusion	368	kJ/kg
Latent heat of vaporisation	5251 ± 251	kJ/kg
Thermal conductivity	156	W/(m °C)
Electrical resistivity at 25°C	44.8	nΩ m
Young's modulus (at 20°C, 99.8% pure Mg)	44.7	GPa

Mg makes **strongly ionic compounds** with common halide, sulfate or phosphate anions as well as making weakly ionic compounds of Mg oxide and nitride.

Mg – abundance in the Earth and mineralogy

- Mg is the **fifth most abundant element** in the **hydrosphere** and the most abundant structural metal ion in the **ocean**. In contrast, Al is only sparingly soluble in the oceans, and is extracted from lithospheric resources only (bauxite).

- In the **upper crust** Mg is the **eighth** most abundant element (**2.5% MgO** wt.). It is an important constituent of major rock-forming minerals, such as pyroxenes and olivine.

- The solid mineral phases from which Mg is extracted from the **lithosphere** are:
  - **Dolomite** $CaMg(CO_3)_2$ ←
  - **Magnesite** $MgCO_3$
  - **Periclase** MgO
  - **Hydromagnesite** $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$
  - **Brucite** $Mg(OH)_2$
  - …and various silicates of Mg, such as **olivine**, **serpentine** and **biotite**.

- The solid mineral phases of hydrospheric origin, found in **evaporite deposits**, are:
  - **Epsomite** $MgSO_4 \cdot 7H_2O$
  - **Kieserite** $MgSO_4 \cdot H_2O$
  - **Langbeinite** $K_2Mg_2(SO_4)_3$
  - **Kainite** $MgSO_4 \cdot KCl \cdot 3H_2O$
  - **Carnallite** $KMgCl_3 \cdot 6H_2O$
  - **Bischofite** $MgCl_2 \cdot 6H_2O$

Mg – major deposit classes

- Of the potential lithospheric sources dolomite is the most commonly used. Alternative sources are **magnesite** and **Mg silicates**.

- In **saline lake water** or **brines** Mg is present at lower concentrations, typically **< 0.7% wt.**, while in the **sea** the Mg content is **0.13% wt**. Two major undesirable components, **water** and **NaCl**, must be removed from these sources before attempting to extract Mg.

Dolomite quarry
(Pennsylvania)

Mg – extraction methods and processing

There are two main routes for making Mg metal:

1. **The electrolytic method** – **Mg chloride** is the feed material to this process. The Mg chloride is derived from **Mg oxide** sources (by chlorination of MgO or magnesite) or from **chloride sources**.

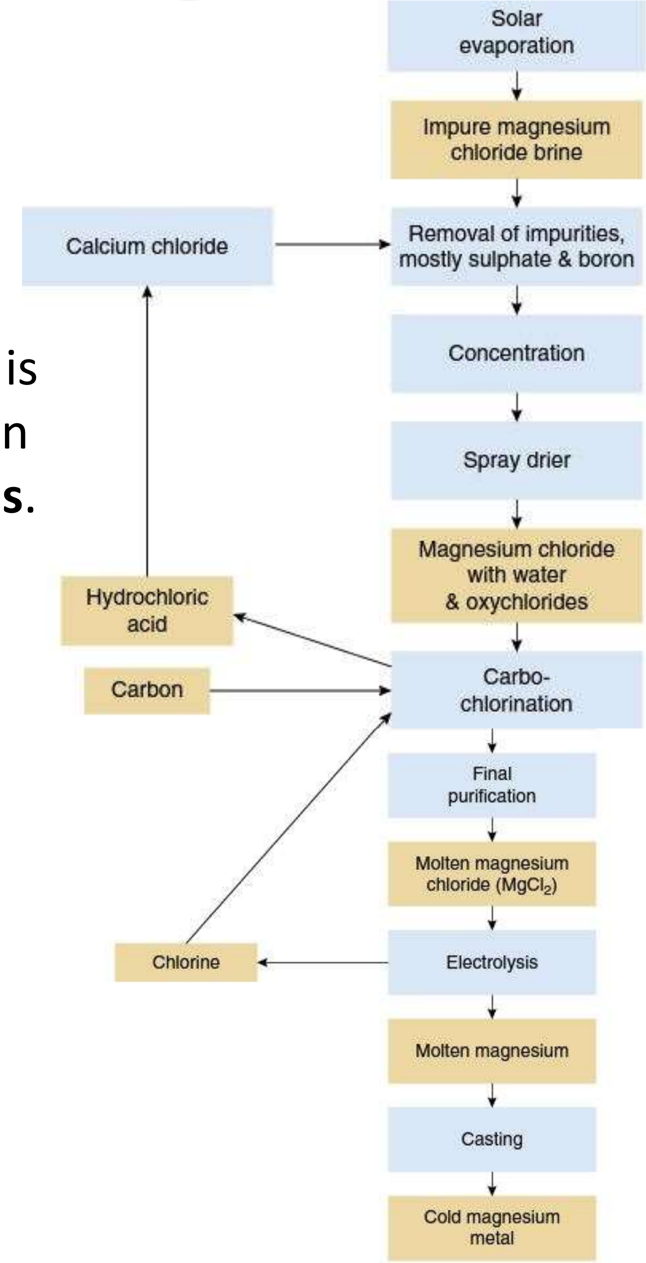


Figure 11.1 Schematic flowsheet for U.S. Magnesium's electrolytic process in Utah. (Modified from Holywell, 2005.)

Mg – extraction methods and processing

2. **Metallothermic reduction** – the **dolomite** feed material is calcined and then reduced, either by Si or one of its alloys, or by other metals such as Al.

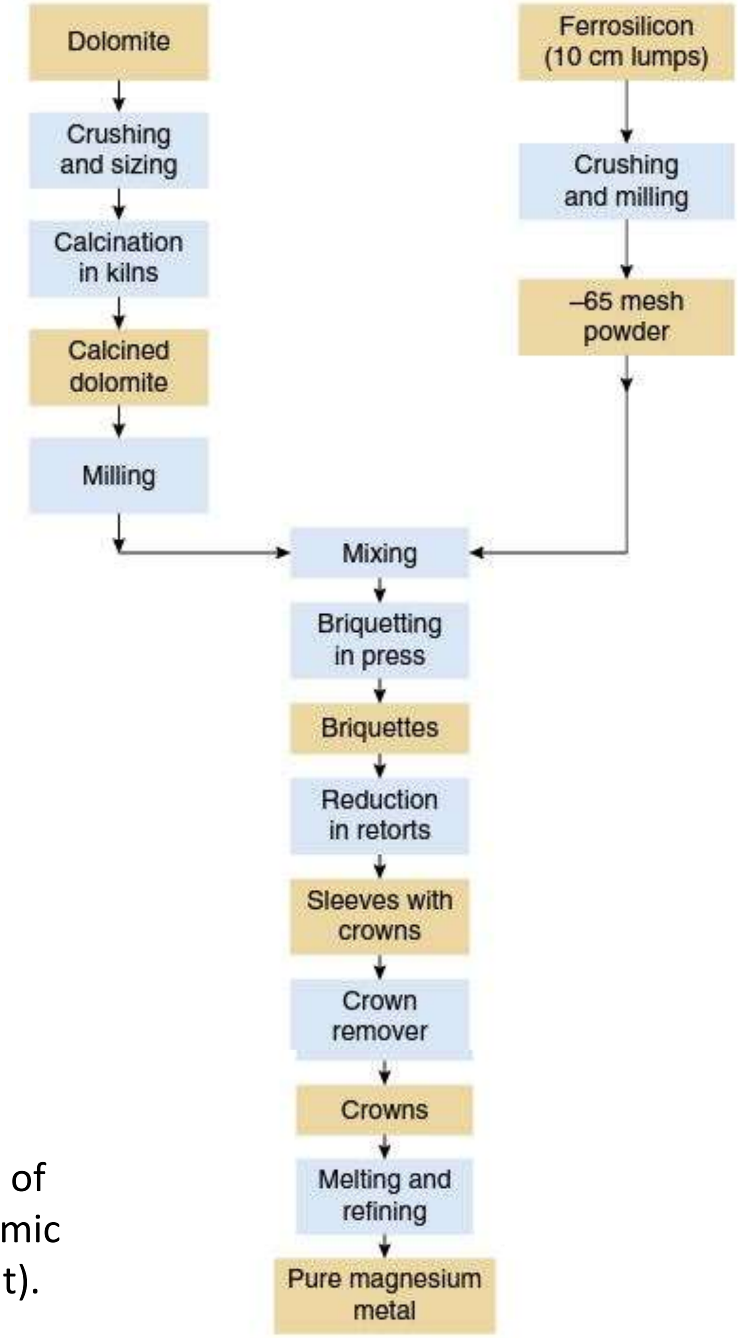


Figure 11.2 Schematic flowsheet for the production of magnesium by the Pidgeon process.

Schematic flowsheet for the production of Mg by the **Pidgeon process** (metallothermic reduction using ferrosilicon as reductant).

Mg – specifications and uses

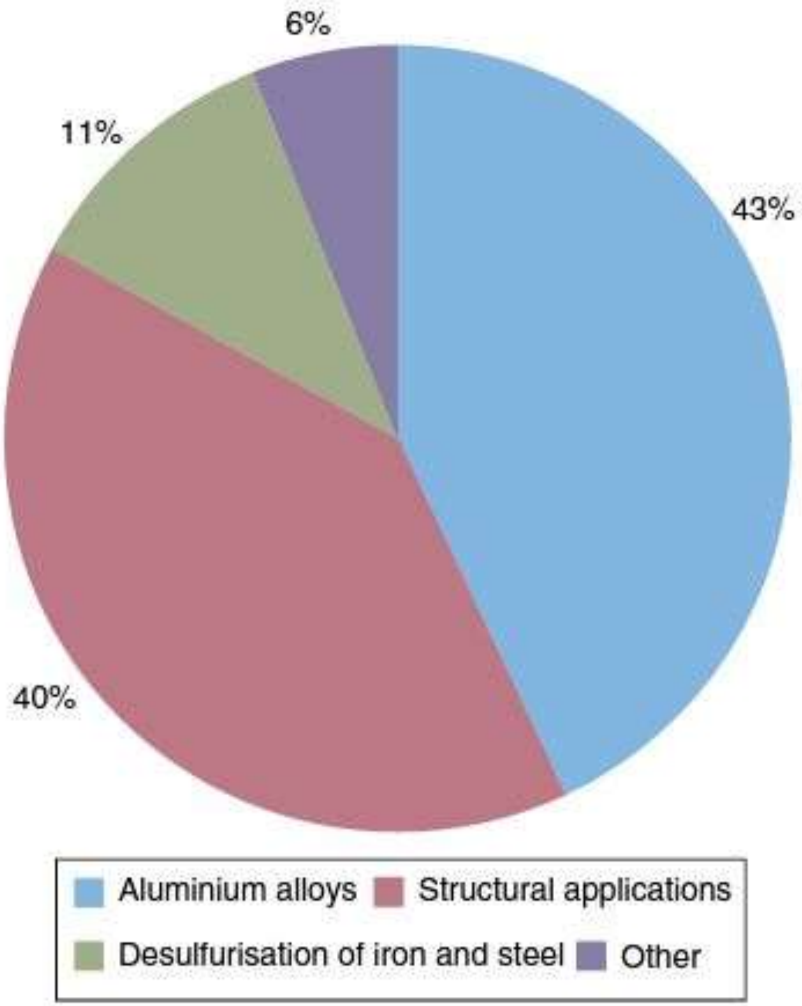


Figure 11.3 The main sectors of magnesium use in the USA in 2011. (Data from United States Geological Survey, 2012.)

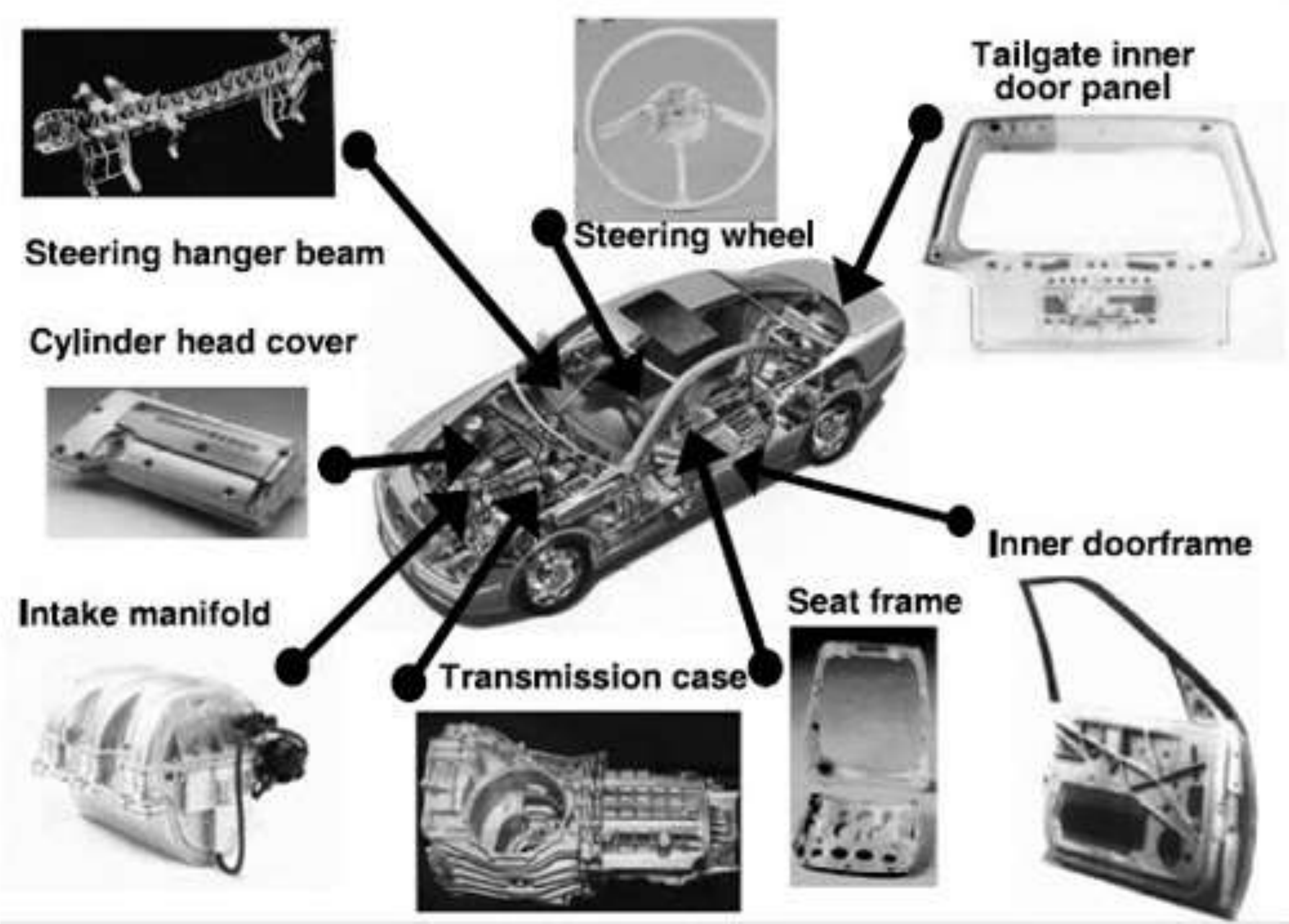
For **structural applications**, Mg is alloyed with other metals to give suitable properties (A=**Al**, M=**Mn**, Z=**Zn**, etc.). Typical casting alloys, such as AM50, AM60 and AZ91 contain 5 to 9% Al, 0.5 to 0.7 Zn, and 0.2 to 0.5 Mn. In terms of volume the largest use of Mg has for many years been as an **additive to impart stiffness to Al alloys** (e.g. Al foil).

Automotive and **3-C** (computers – cameras – communications) **industries**. E.g. VW Beetle Mg transmission and engine block, aircraft engine bearers (WW II).

Military applications: plates in military armour, signal system electronics, radio machinery. Mg powder → MRE (Mg ready to eat) food warming.

Mg powder for the **reduction of S content** of molten Fe (high electronegativity of Mg). Preferred **reducing agent** for Ti, Zr, U and Be from the respective chlorides or fluorides.

Mg – automotive industry



Mg – recycling

- **Recycling**: Mg is **easily recycled** in many of its primary forms, and is also capable of being recycled from secondary sources when it appears as an alloy with Al. production of primary Mg using an electrolytic process can consume up to 35 kWh/kg, whereas re-melting Mg metal scrap uses **less than 10%** of the energy used to make primary metal. The recycling of Al cans (Mg≈ 2% wt.) has become a highly technical and controlled process.

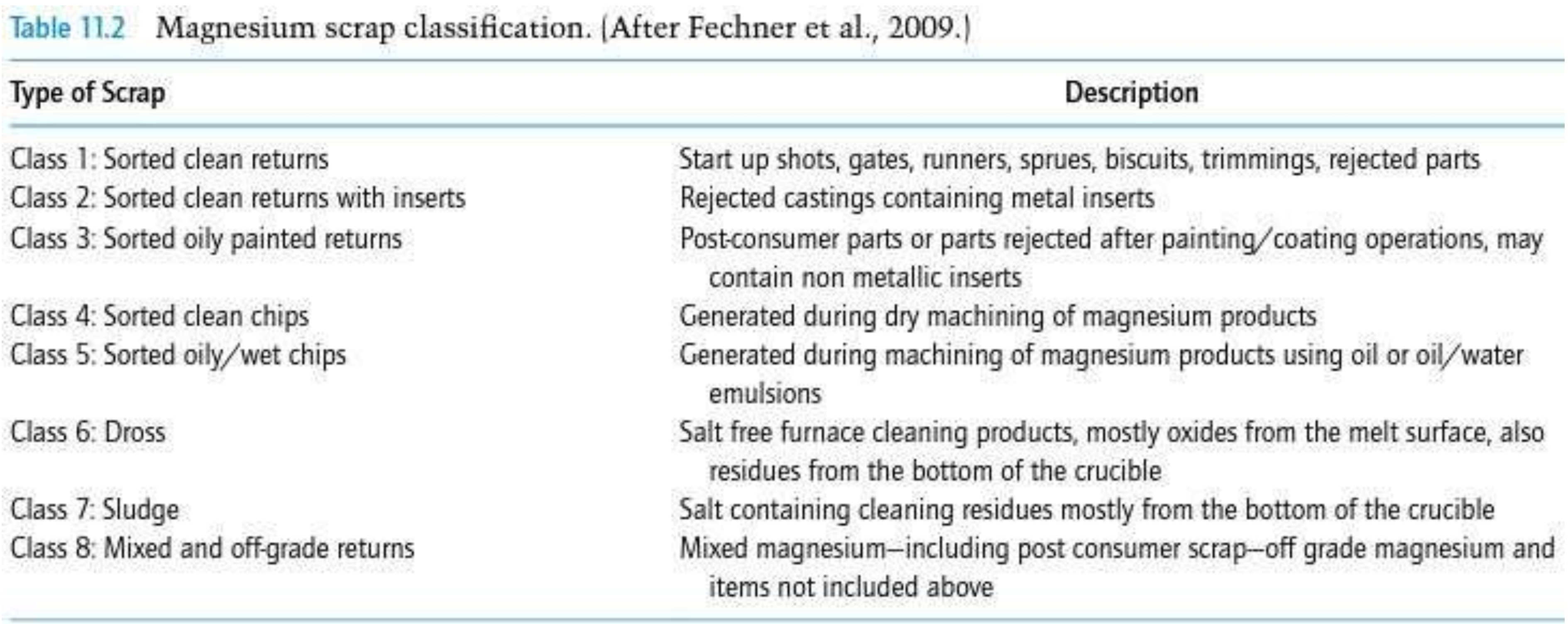


Table 11.2 Magnesium scrap classification. (After Fechner et al., 2009.)

Type of Scrap	Description
Class 1: Sorted clean returns	Start up shots, gates, runners, sprues, biscuits, trimmings, rejected parts
Class 2: Sorted clean returns with inserts	Rejected castings containing metal inserts
Class 3: Sorted oily painted returns	Post-consumer parts or parts rejected after painting/coating operations, may contain non metallic inserts
Class 4: Sorted clean chips	Generated during dry machining of magnesium products
Class 5: Sorted oily/wet chips	Generated during machining of magnesium products using oil or oil/water emulsions
Class 6: Dross	Salt free furnace cleaning products, mostly oxides from the melt surface, also residues from the bottom of the crucible
Class 7: Sludge	Salt containing cleaning residues mostly from the bottom of the crucible
Class 8: Mixed and off-grade returns	Mixed magnesium–including post consumer scrap–off grade magnesium and items not included above

Mg – substitution

- Mg alloys are used in many applications including the **aerospace**, **automotive** and the **3-C** industries. The properties of Mg, such as its **strength-to-weight ratio**, its **low fabrication costs**, **electromagnetic shielding**, **thermal** and **electrical conductivity** and **damping** characteristics → difficult to find a direct substitute for Mg.

- Potential problems when Mg components are being joined by choosing fasteners with **similar thermal expansion coefficients**, such as Al and Mg. Steel fasteners → **galvanic corrosion** and **creep** issues.

Mg – production

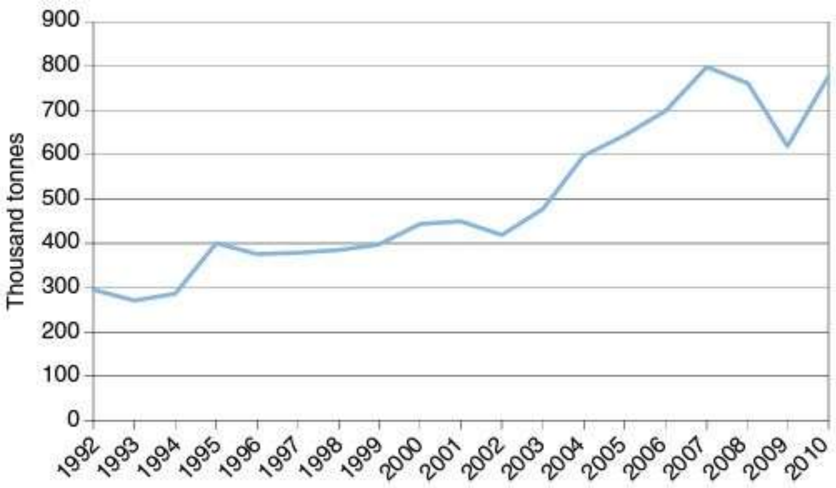


Figure 11.4 World production of magnesium metal, 1992–2010. (Data from British Geological Survey World Mineral Statistics database.)

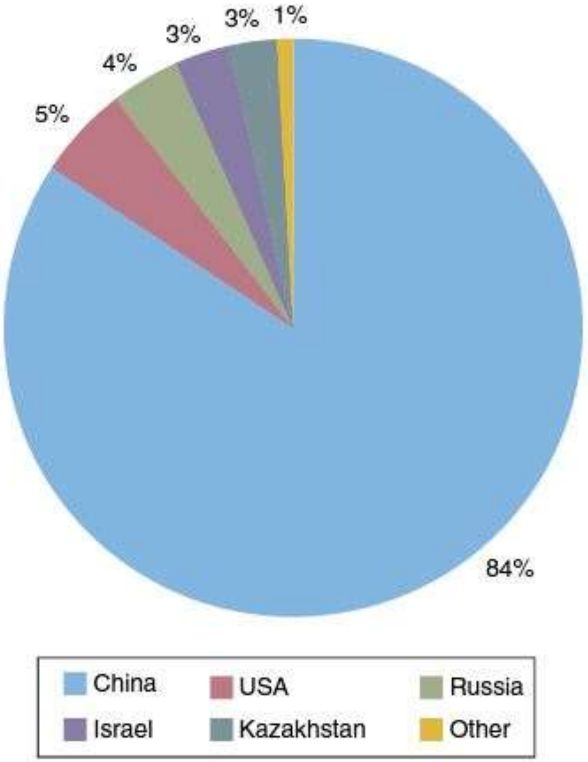
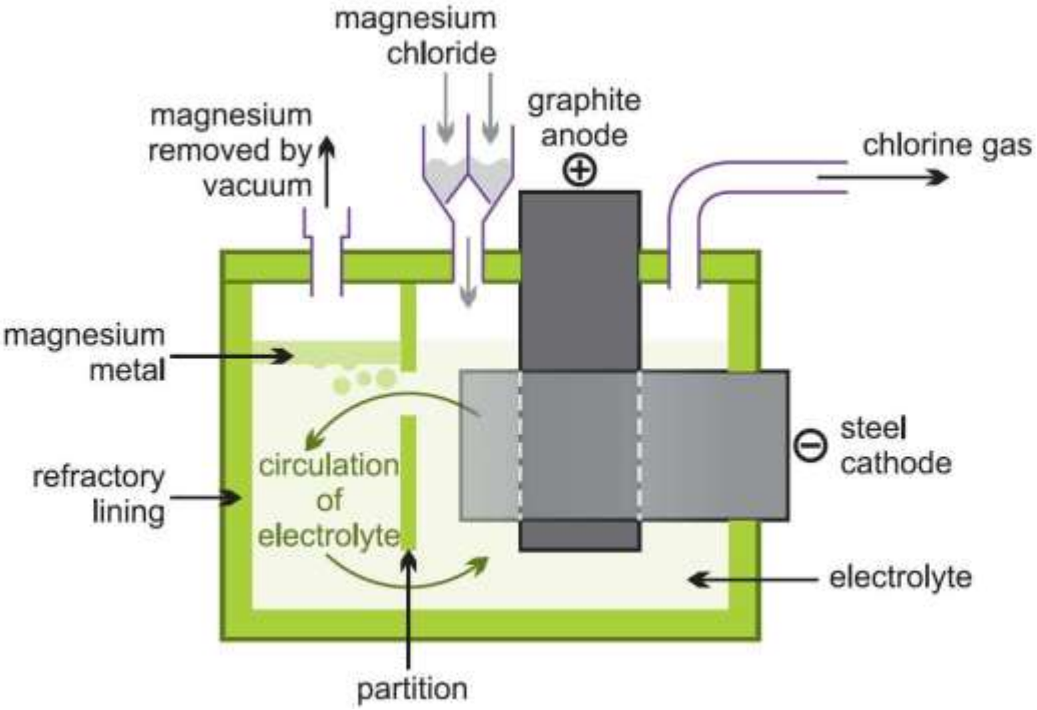


Figure 11.5 World production of magnesium metal by country in 2010. (Data from British Geological Survey, 2012.)



Mg – prices

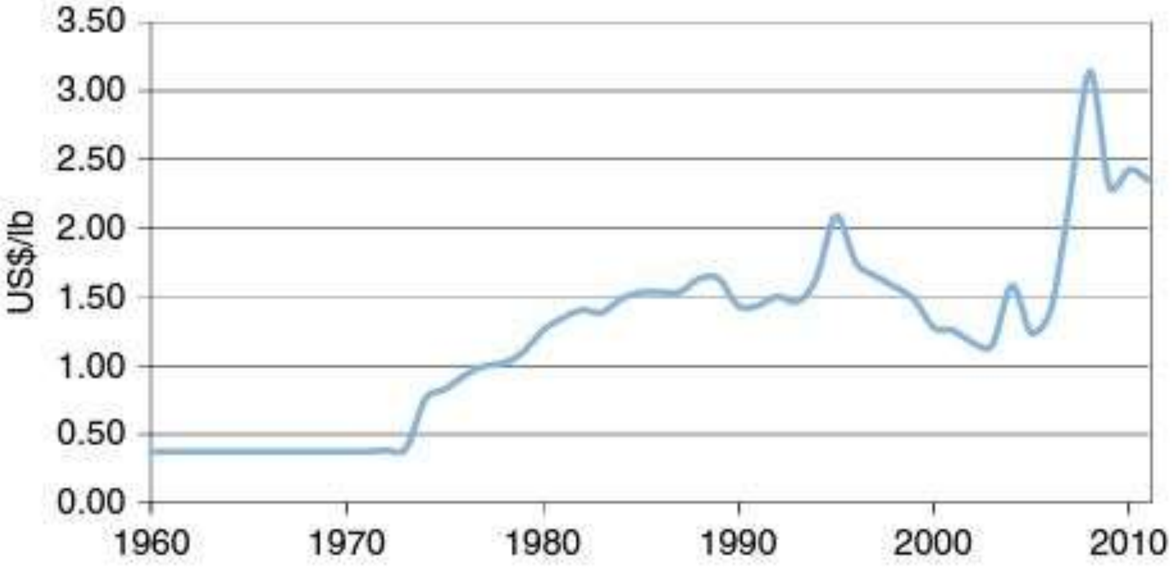


Figure 11.8 Year-end prices of magnesium in USA, 1960 – 2011. (Prices are U.S. spot Western price for 99.8%-pure magnesium ingot, compiled from United States Geological Survey (1999) for 1960–1998, and from United States Geological Survey Annual Mineral Commodity Summaries for 1999 to 2011.)

Mg – exporting countries

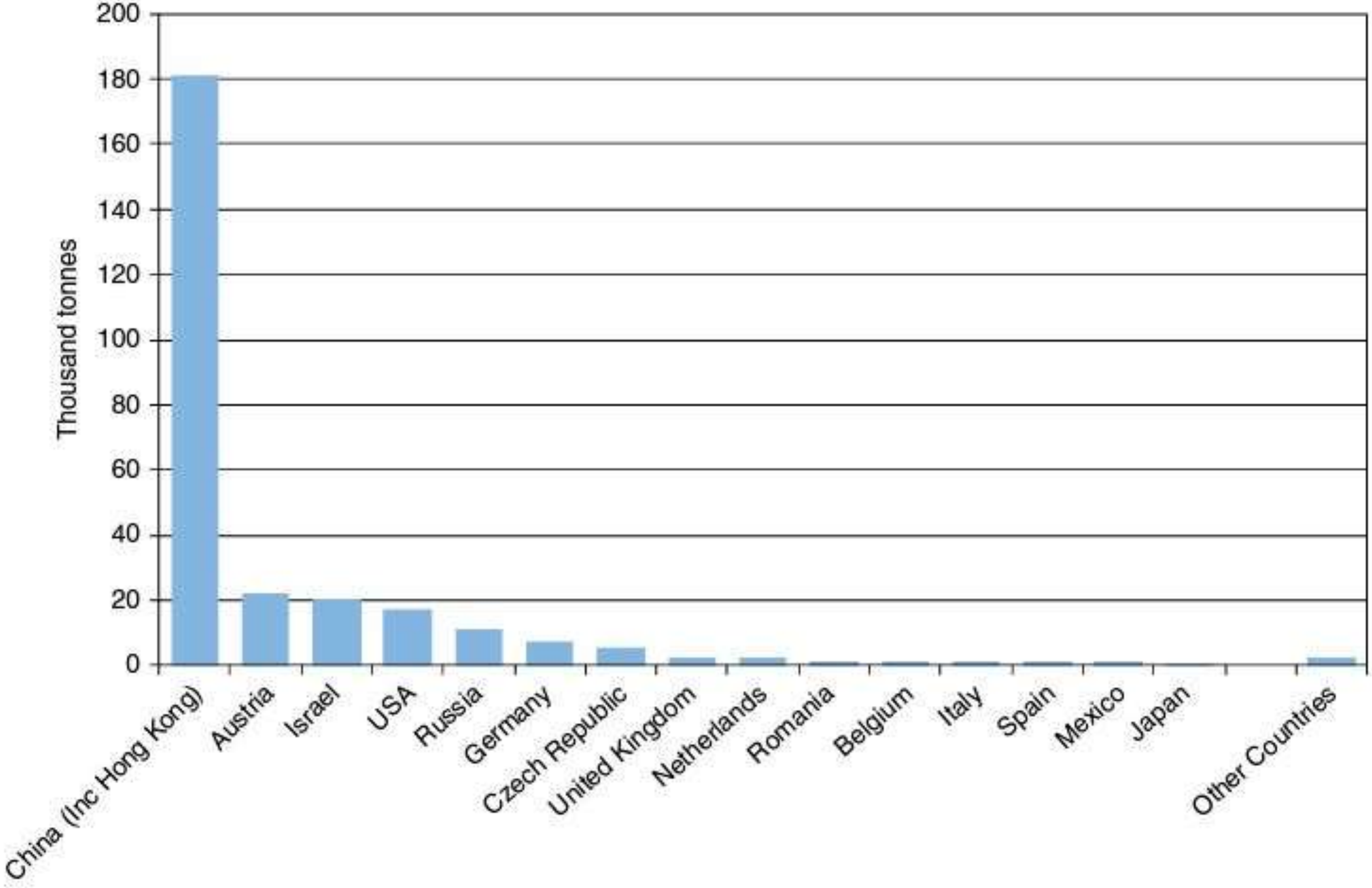


Figure 11.7 The top exporting countries of magnesium metal in 2009. (Data from British Geological Survey World Mineral Statistics database and UN Comtrade, 2013.)

Mg – importing countries

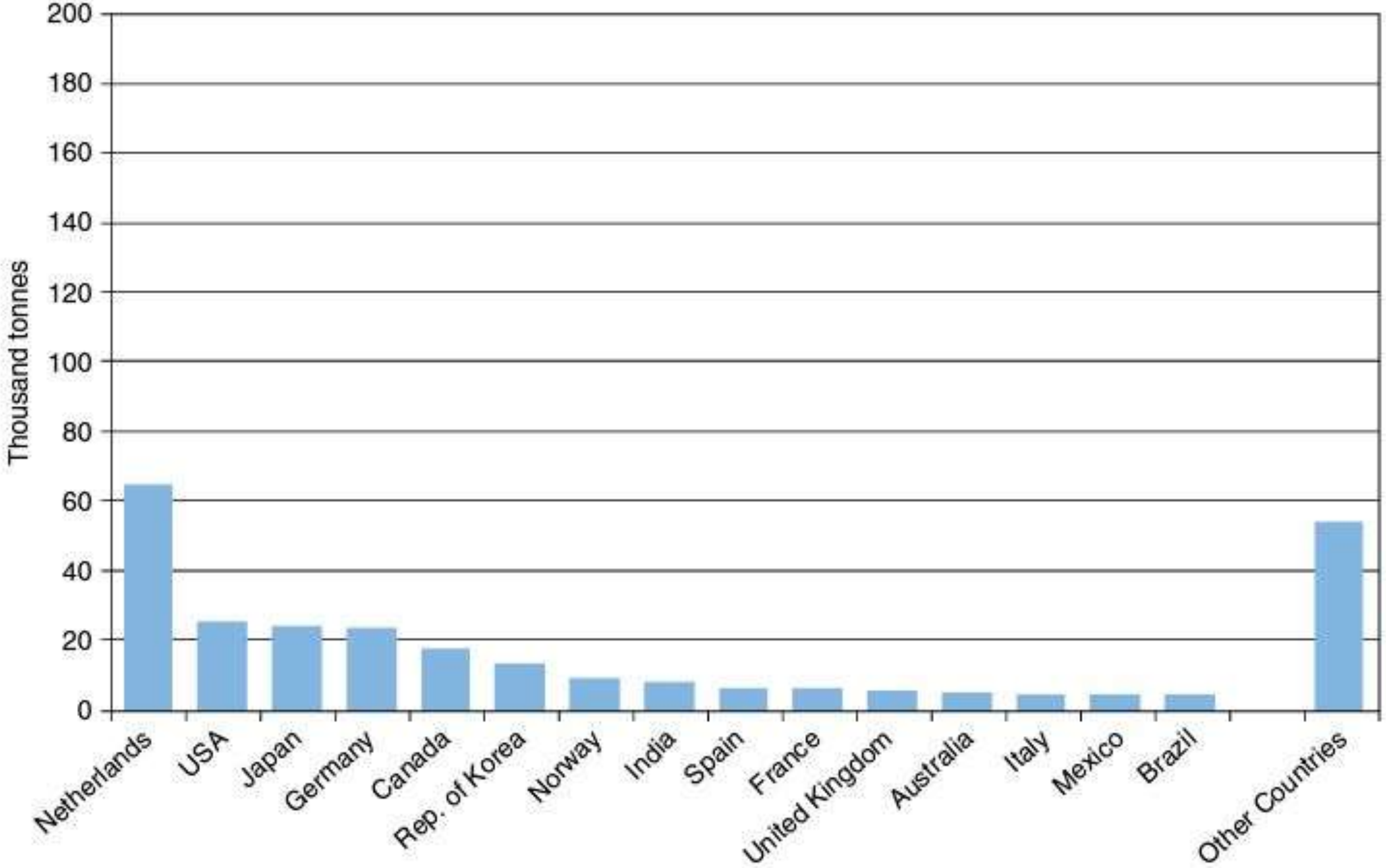


Figure 11.6 The top importing countries of magnesium metal in 2009. (Data from British Geological Survey World Mineral Statistics database and UN Comtrade, 2013.)

Mg – environmental issues

- As the **lightest available structural metal**, the use of Mg provides the benefit of **reducing the weight** of automobiles and thereby **reduces fuel consumption**.

- Benefits from the use of Mg in **reducing CO_2 emissions.**

- The climate control aspects of GHG (“Greenhouse Gases”) release to the atmosphere from metal production has already prompted producers to use sulfur dioxide and other reagents instead of **sulfur hexafluoride SF_6** to provide the cover gas used in the production of Mg alloys.

- Raw materials used in making Mg (except **chrysotile-bearing** tailings) are **non toxic**.

- All plants have Mg in the center of the **chlorophyll** molecule, essential for the photosynthesis → Mg is a common additive to **fertilizers**.

- Mg is also important to all **living cells** where it plays a major role in the functioning of numerous **enzymes**.

Mg – life-cycle inventory

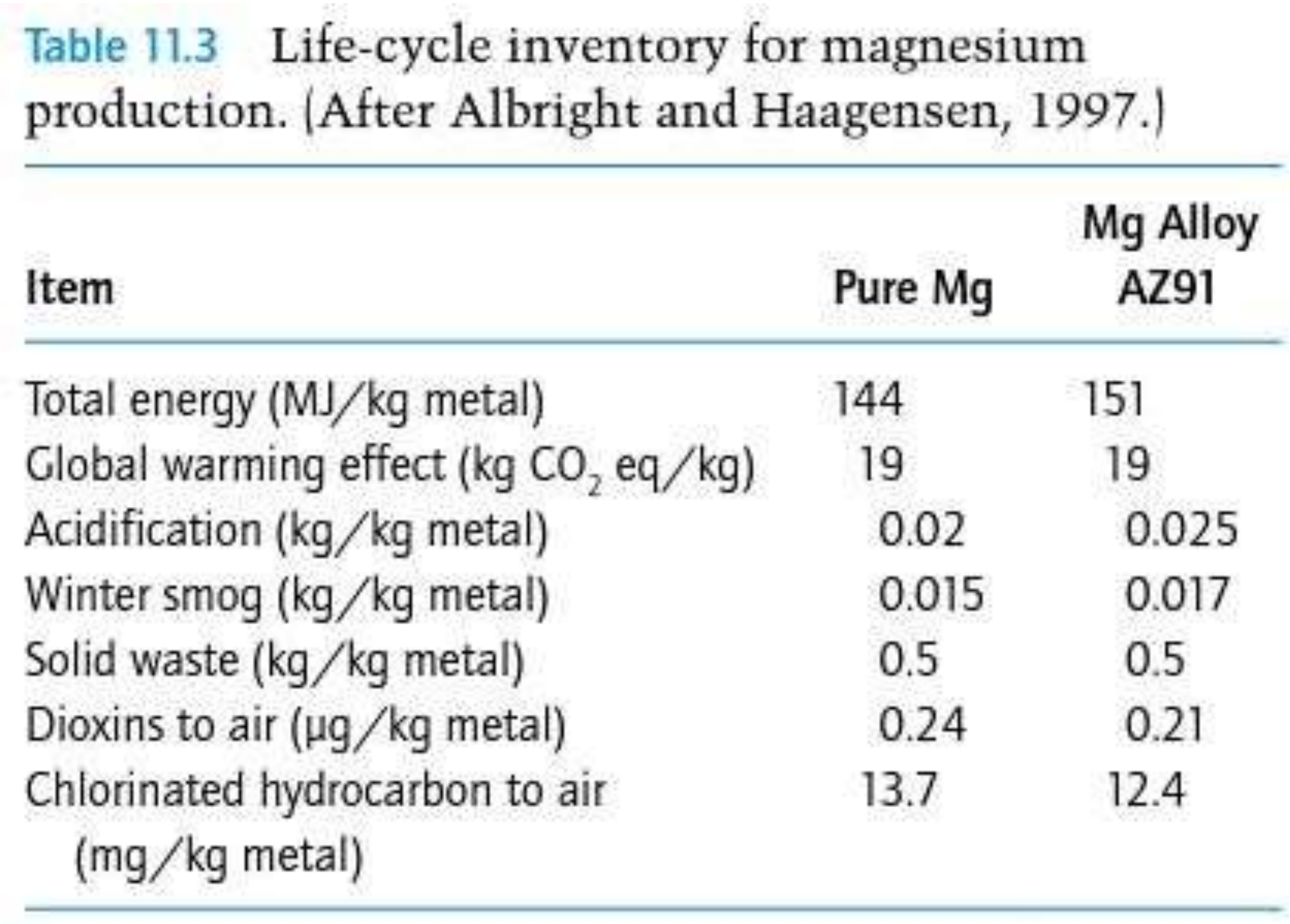


Table 11.3 Life-cycle inventory for magnesium production. (After Albright and Haagensen, 1997.)

Item	Pure Mg	Mg Alloy AZ91
Total energy (MJ/kg metal)	144	151
Global warming effect (kg CO_2 eq/kg)	19	19
Acidification (kg/kg metal)	0.02	0.025
Winter smog (kg/kg metal)	0.015	0.017
Solid waste (kg/kg metal)	0.5	0.5
Dioxins to air (μg/kg metal)	0.24	0.21
Chlorinated hydrocarbon to air (mg/kg metal)	13.7	12.4

Mg – outlook

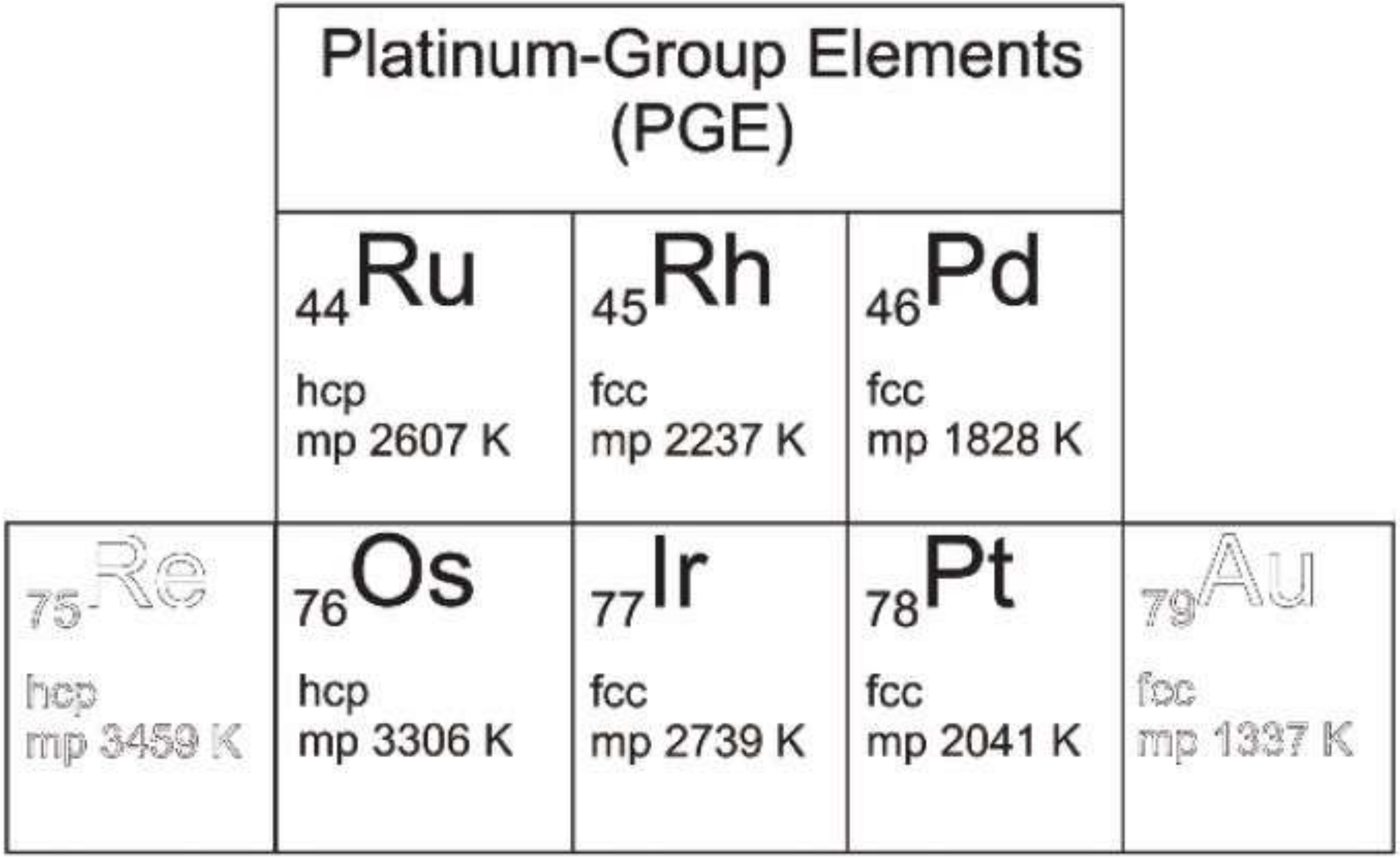
- There is continuing international research and development into **reducing the GHG emissions** associated with the production of Mg. In China, while the old **Pidgeon process** produced emissions of about **36 kg CO_2** per Kg of Mg, this is being reduced to abut **20 kg CO_2** per kg of Mg by better energy management. In contrast, the **electrolytic** Mg plant in Canada, which was operated with hydroelectric power and used magnesite as the starting material, produced **6.9 kg CO_2** per kg of Mg.

- **Alternative raw materials**, such as **sulfate minerals** are currently being investigated.

- Governments and industry worldwide are currently funding major research programmes into developing **new uses of Mg**.

PGM – Platinum group metals

PGM – Platinum group metals



	Platinum-Group Elements (PGE)			
	$_{44}$Ru hcp mp 2607 K	$_{45}$Rh fcc mp 2237 K	$_{46}$Pd fcc mp 1828 K	
$_{75}$Re hcp mp 3459 K	$_{76}$Os hcp mp 3306 K	$_{77}$Ir fcc mp 2739 K	$_{78}$Pt fcc mp 2041 K	$_{79}$Au fcc mp 1337 K

FIGURE 2 A portion of the periodic table containing the highly siderophile elements, which includes the platinum-group elements, rhenium, and gold. Elements are depicted with their atomic number, crystal structure, and melting point. COURTESY OF H. PALME

PGM – definitions and characteristics

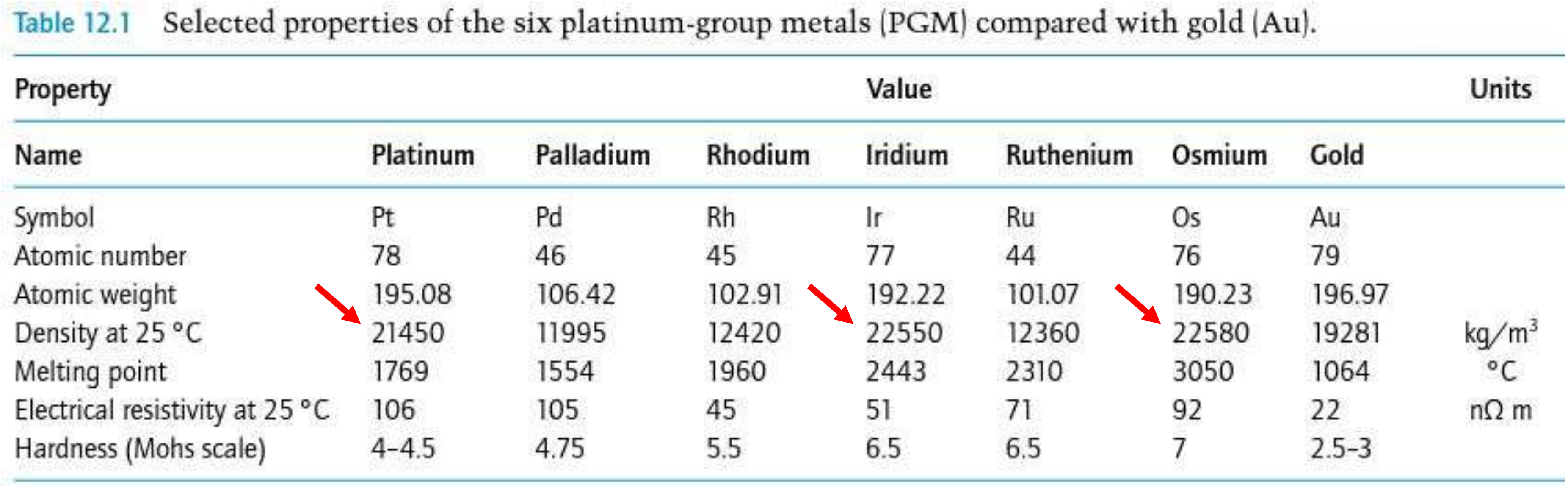


Table 12.1 Selected properties of the six platinum-group metals (PGM) compared with gold (Au).

Property				Value				Units
Name	**Platinum**	**Palladium**	**Rhodium**	**Iridium**	**Ruthenium**	**Osmium**	**Gold**	
Symbol	Pt	Pd	Rh	Ir	Ru	Os	Au	
Atomic number	78	46	45	77	44	76	79	
Atomic weight	195.08	106.42	102.91	192.22	101.07	190.23	196.97	
Density at 25 °C	21450	11995	12420	22550	12360	22580	19281	kg/m^3
Melting point	1769	1554	1960	2443	2310	3050	1064	°C
Electrical resistivity at 25 °C	106	105	45	51	71	92	22	nΩ m
Hardness (Mohs scale)	4–4.5	4.75	5.5	6.5	6.5	7	2.5-3	

- The **PGM** (**Platinum-group metals**) are rare precious metals, although unlike Au, they are used in a diverse range of **industrial applications** as well as in **jewelry**.
- Today, **Pt** and **Pd** are the most commercially important of the PGM, with their largest application being in the automotive industry (**catalysts**).
- **Rh**, which is also used in autocatalysts, is the third most important PGM. **Ru** and **Ir** are used in smaller amounts although they are becoming increasingly important in a variety of new technologies such as **data storage**, **medical implants** and **renewable energy**.
- The name platinum is derived from the Spanish "***platina***", meaning little silver. Archaeological evidence indicates that there is a very long history in of Pt working in South America.
- **Pd** was discovered in 1803 by the English chemist William Hyde Wollaston. It was named after the asteroid *Pallas*, identified in 1801, named after the Greek goddess of wisdom.

“Platina”

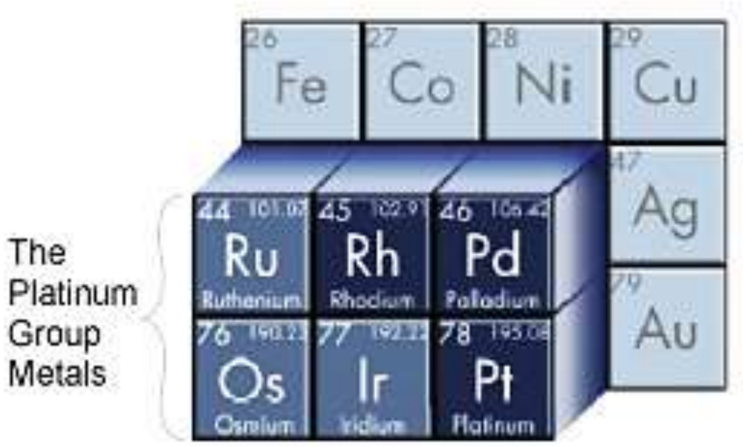
Samples of “platina” recovered from the placer deposits in the Choco district of Colombia. Similar material was described by William Lewis to the Royal Society of London in 1754 and served as the feedstock for the first purification of Pt, Pd, Ir, and Os by Smithson Tennant and William Wollaston. The field of view is 5 cm wide (each nugget is about 3–5 mm in length). Sample is from the mineralogy collection of the Museum National d’Histoire Naturelle (#4.283; Picture D. Brabant, MNHN). PHOTO COURTESY OF JEAN-PIERRE LORAND

Palladium

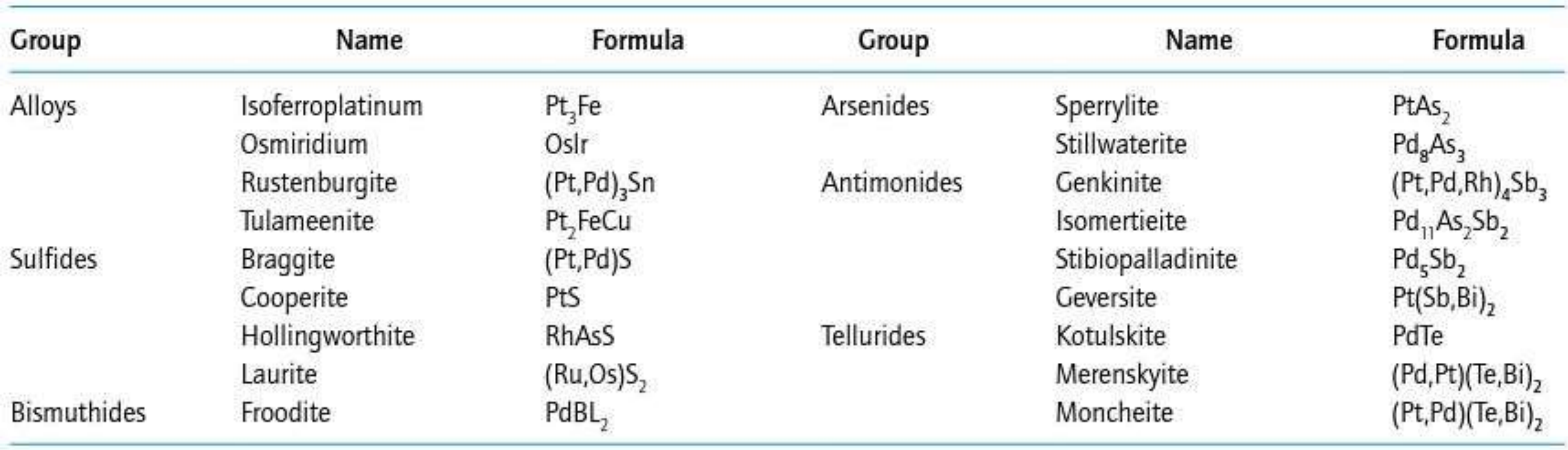
Front and back faces of the Wollaston Medal presented to Sir William Logan (first director of the Geological Survey of Canada) in 1856. The front of the medal depicts William Wollaston, the benefactor of the award. The medal is cast in palladium, which Wollaston discovered in 1805. The Wollaston Medal is the highest award bestowed by the Geological Society of London. NATURAL RESOURCES CANADA IMAGE NRCAN-4374, USED WITH PERMISSION OF NATURAL RESOURCES CANADA. HER MAJESTY THE QUEEN IN RIGHT OF CANADA

PGM – definitions and characteristics

- The **PGM** are **transition metals**, which together with Fe, Co and Ni are found in Groups 8, 9 and 10 of the Periodic Table.
- **Os**, **Ir** and **Ru** are sometimes referred to as the **IPGM** (**Ir sub-group**), and **Pt**, **Pd** and **Rh** as the **PPGM** (**Pd sub-group**), on account of their similar geochemical behavior under magmatic conditions.
- All six PGM are chemically similar with strong **siderophile** and **chalcophile** tendencies, preferentially bonding with **Fe**, **Ni**, **Cu** and **S** rather than with O. The distribution of PGM in the Earth is thus controlled by the presence of metallic phases, being strongly concentrated in the Earth's core after planetary accretion.
- They do not dissolve in strong acids, but they do **react with O at high T** to form volatile oxides. The physical properties of the PGM vary considerably, but all display properties typical of metals, including the **ability to form alloys**, to **conduct heat** and **electricity**, and some degree of **malleability** and **ductility**.
- **Pt**, **Ir** and **Os** are the **densest known metals**. Pt and Pd are **highly resistant to heat** and to **corrosion**, and are soft and ductile. **Rh** and **Ir** are more difficult to work, **Ru** and **Os** are hard, brittle and almost unworkable.
- All PGM, commonly alloyed with one another or with other metals, can act as **catalysts** in a wide range of industrial applications.



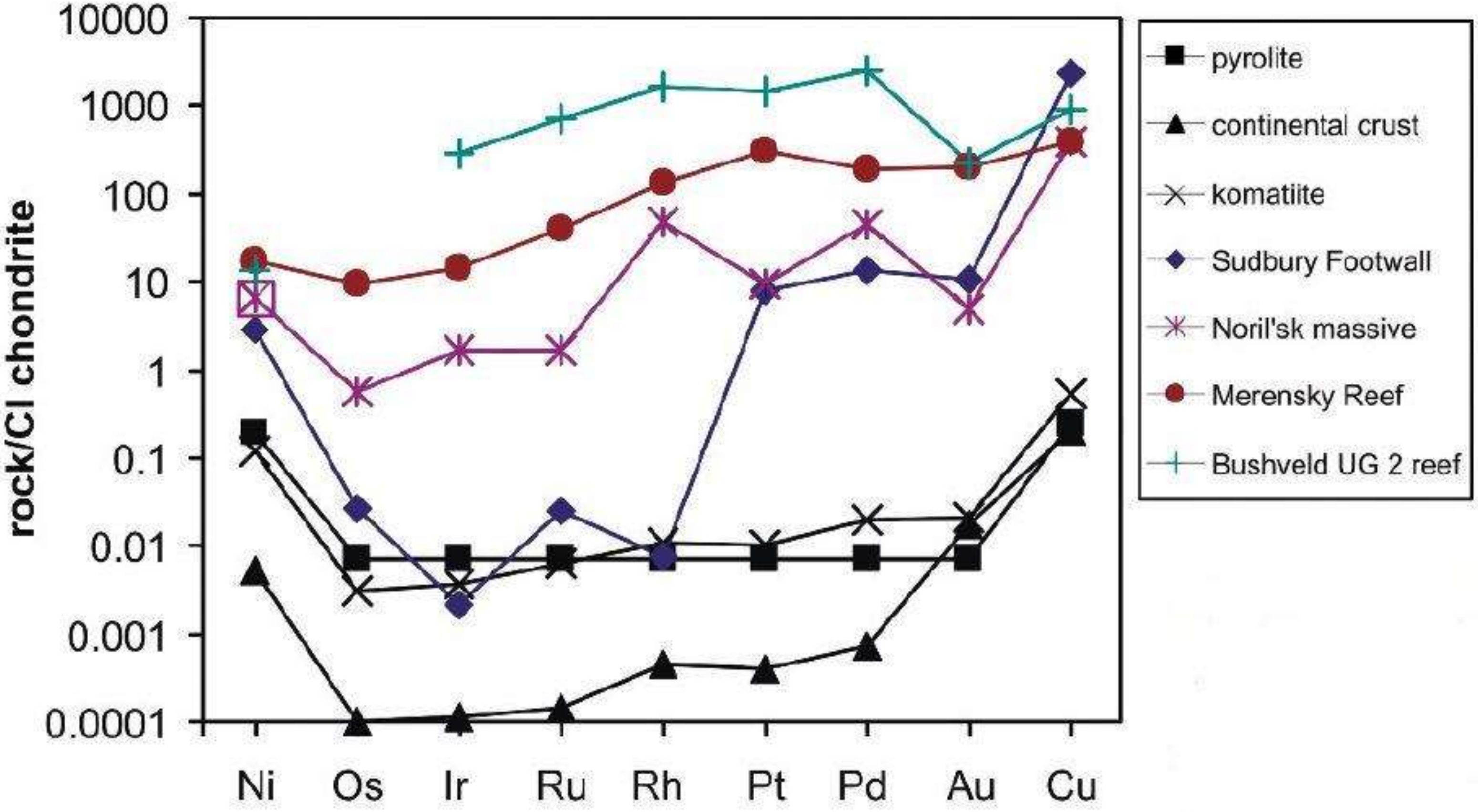
PGM – abundance in the Earth and mineralogy



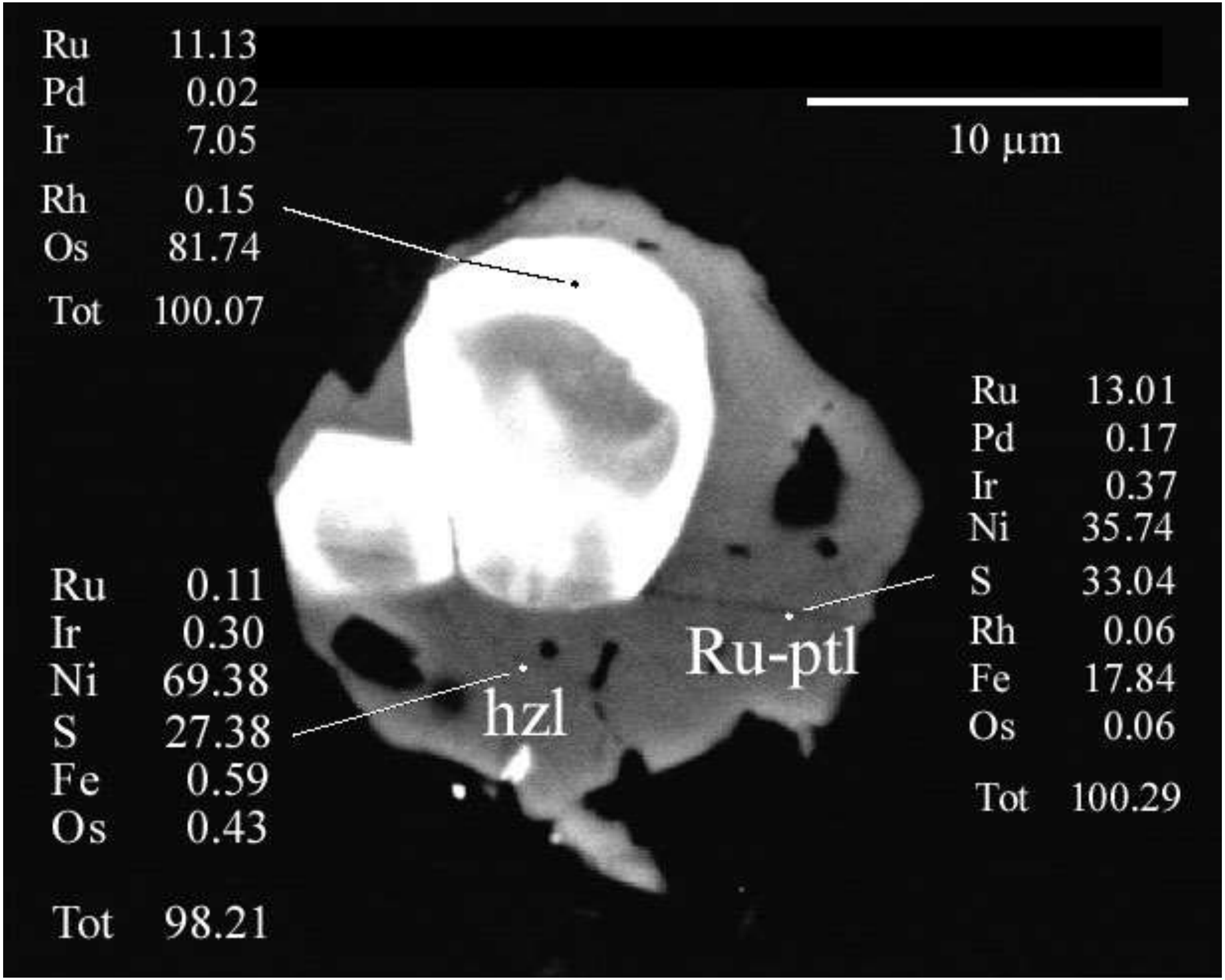
Group	Name	Formula	Group	Name	Formula
Alloys	Isoferroplatinum	Pt_3Fe	Arsenides	Sperrylite	$PtAs_2$
	Osmiridium	$OsIr$		Stillwaterite	Pd_8As_3
	Rustenburgite	$(Pt,Pd)_3Sn$	Antimonides	Genkinite	$(Pt,Pd,Rh)_4Sb_3$
	Tulameenite	Pt_2FeCu		Isomertieite	$Pd_{11}As_2Sb_2$
Sulfides	Braggite	$(Pt,Pd)S$		Stibiopalladinite	Pd_5Sb_2
	Cooperite	PtS		Geversite	$Pt(Sb,Bi)_2$
	Hollingworthite	$RhAsS$	Tellurides	Kotulskite	$PdTe$
	Laurite	$(Ru,Os)S_2$		Merenskyite	$(Pd,Pt)(Te,Bi)_2$
Bismuthides	Froodite	$PdBL_2$		Moncheite	$(Pt,Pd)(Te,Bi)_2$

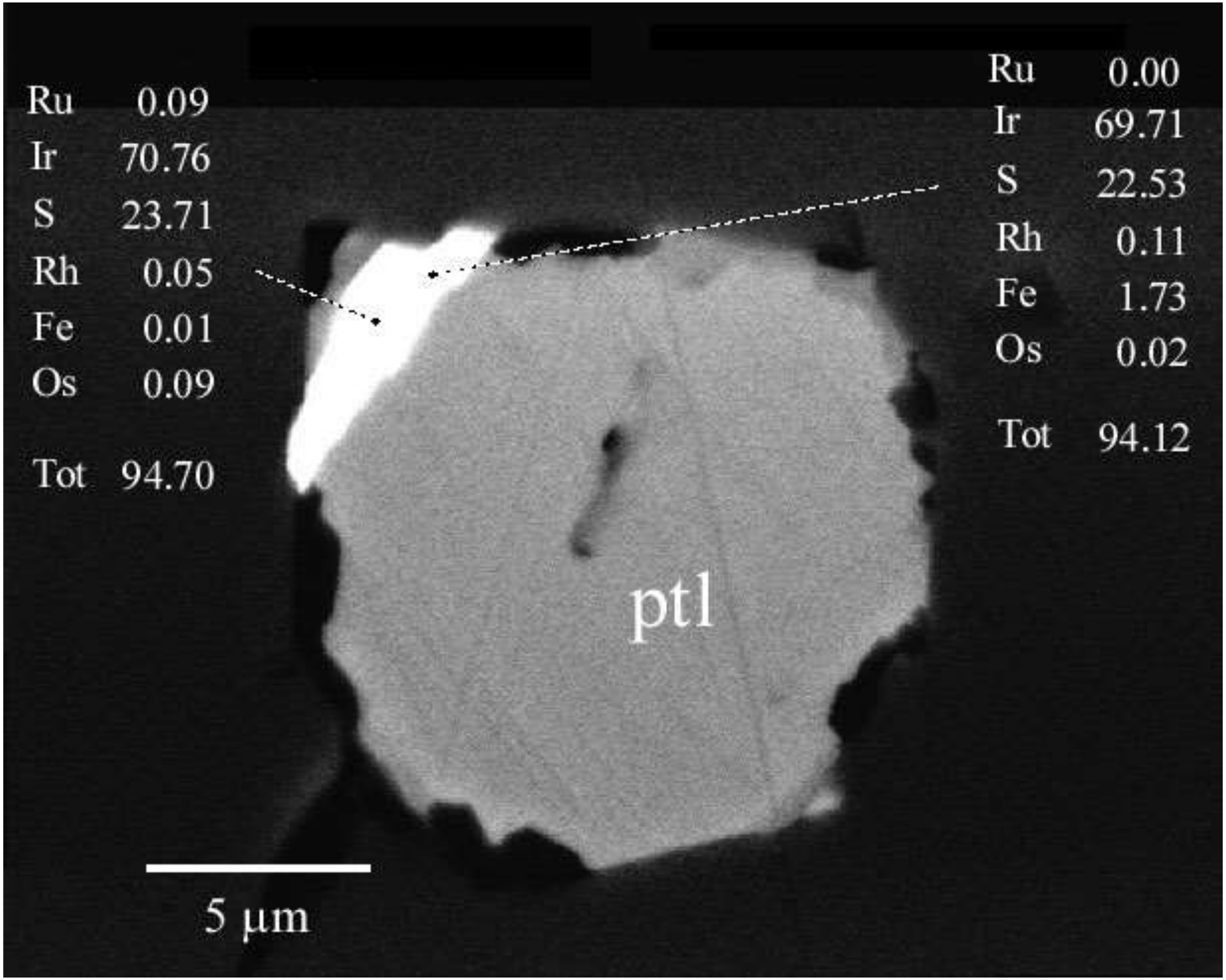
- The PGM are very rare in the Earth's crust, with **Pt** and **Pd** present at similar concentrations of approximately **5 ppb**. **Rh**, **Ir** and **Ru** are even scarcer at about **1 ppb**.
- Relative to other rock types the PGM are enriched in **ultramafic lithologies**, such as peridotite, in which Pt and Pd concentrations are commonly **10 – 20 ppb**.
- In nature, the PGM are chiefly held either **in base-sulfide minerals**, such as **pyrrhotite**, **chalcopyrite** and **pentlandite**, or in **PGM-bearing accessory minerals**.
- The PGM rarely occur as native metal but commonly form a wide variety of **alloys** with one another or with other metals, notably with **Fe**, and less commonly with Sn, Cu, Pb, Hg and Ag. In other platinum-group minerals the PGM are bonded to **S**, **As**, **Sb**, **Te**, **Bi** and **Se**.

PGM – abundance in the Earth



Compositions of major Earth reservoirs and the principal ore deposits of PGE (recalculated to 100% sulfide) shown as the concentrations of chalcophile metals normalized to those in CI chondrites. Core formation has stripped most of the PGE from the mantle (pyrolite). The formation of continental crust from the mantle has led to even greater impoverishment; it is primarily by high-degree partial melting of mantle rock that PGE-rich magnesian magmas like komatiite can form. The Merensky Reef approaches the maximum possible PGE enrichment in sulfide melts; the sulfide in the UG-2 has probably been enriched by secondary processes. DATA FROM NALDRETT (2004) AND SOURCES THEREIN


Ru 11.13
Pd 0.02
Ir 7.05
Rh 0.15
Os 81.74
Tot 100.07
10 µm
Ru 13.01
Pd 0.17
Ir 0.37
Ni 35.74
S 33.04
Rh 0.06
Fe 17.84
Os 0.06
Tot 100.29
Ru-ptl
hzl
Ru 0.11
Ir 0.30
Ni 69.38
S 27.38
Fe 0.59
Os 0.43
Tot 98.21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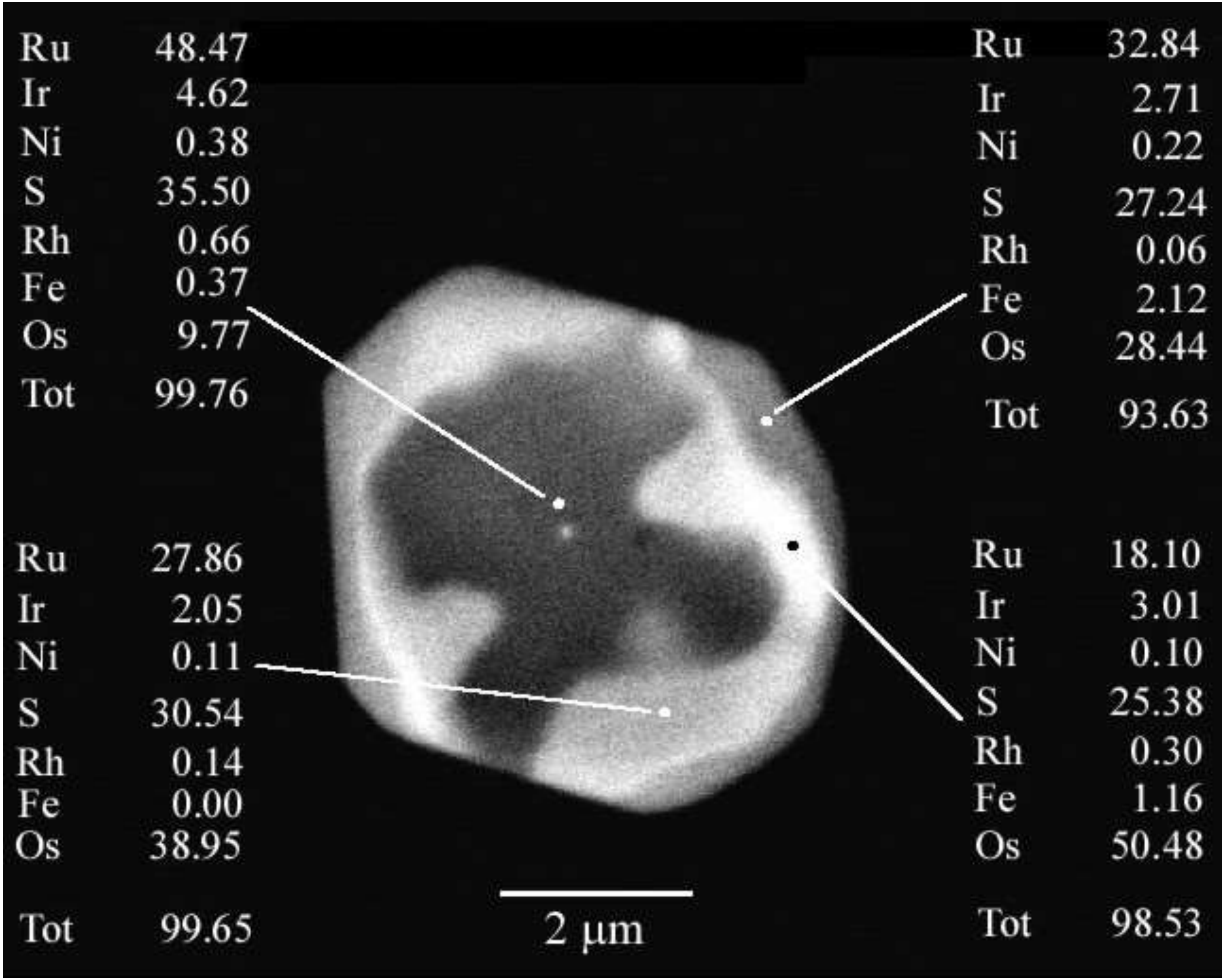


[redacted]

Ru	48.47
Ir	4.62
Ni	0.38
S	35.50
Rh	0.66
Fe	0.37
Os	9.77
Tot	99.76

Ru	32.84
Ir	2.71
Ni	0.22
S	27.24
Rh	0.06
Fe	2.12
Os	28.44
Tot	93.63

Ru	27.86
Ir	2.05
Ni	0.11
S	30.54
Rh	0.14
Fe	0.00
Os	38.95
Tot	99.65

Ru	18.10
Ir	3.01
Ni	0.10
S	25.38
Rh	0.30
Fe	1.16
Os	50.48
Tot	98.53

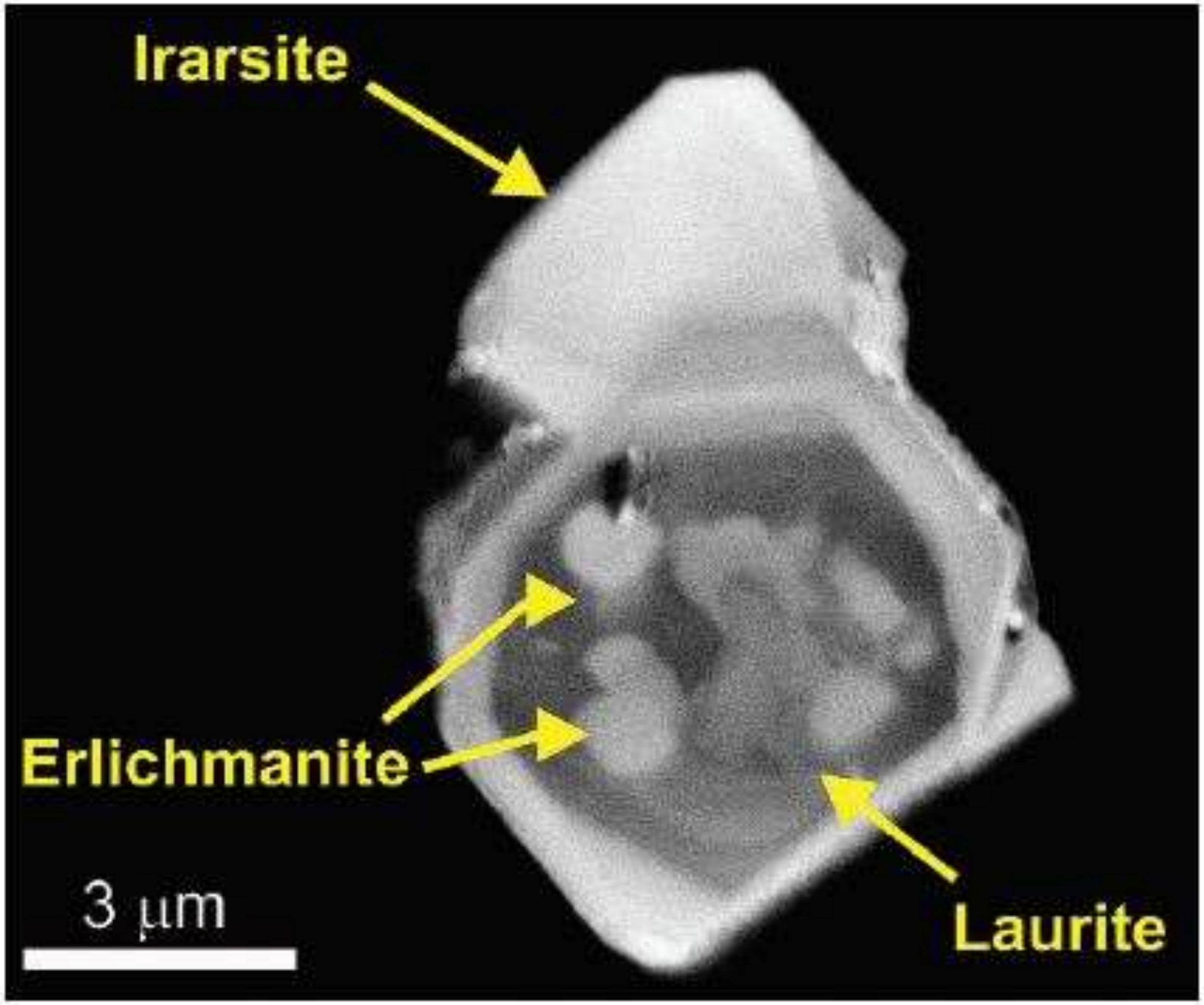


FIGURE 7 Backscattered-electron image depicting an aggregate of platinum-group minerals included in a chromite grain from the Mayarí-Baracoa ophiolite belt of eastern Cuba. The inclusion consists of distinct grains of irarsite (IrAsS) and laurite (RuS_2). The laurite contains a core of Ru-rich erlichmanite (OsS_2) surrounded by a layer of Os-poor laurite grading to Os-rich laurite at the rim. USED WITH PERMISSION FROM SPRINGER SCIENCE+BUSINESS MEDIA: GERVILLA ET AL. (2005; FIG. 4G)

PGM – major deposit classes

- Enrichment of PGM occurs in deposits of several types developed in a **limited range of geological settings**, commonly associated with **Ni** and **Cu**.

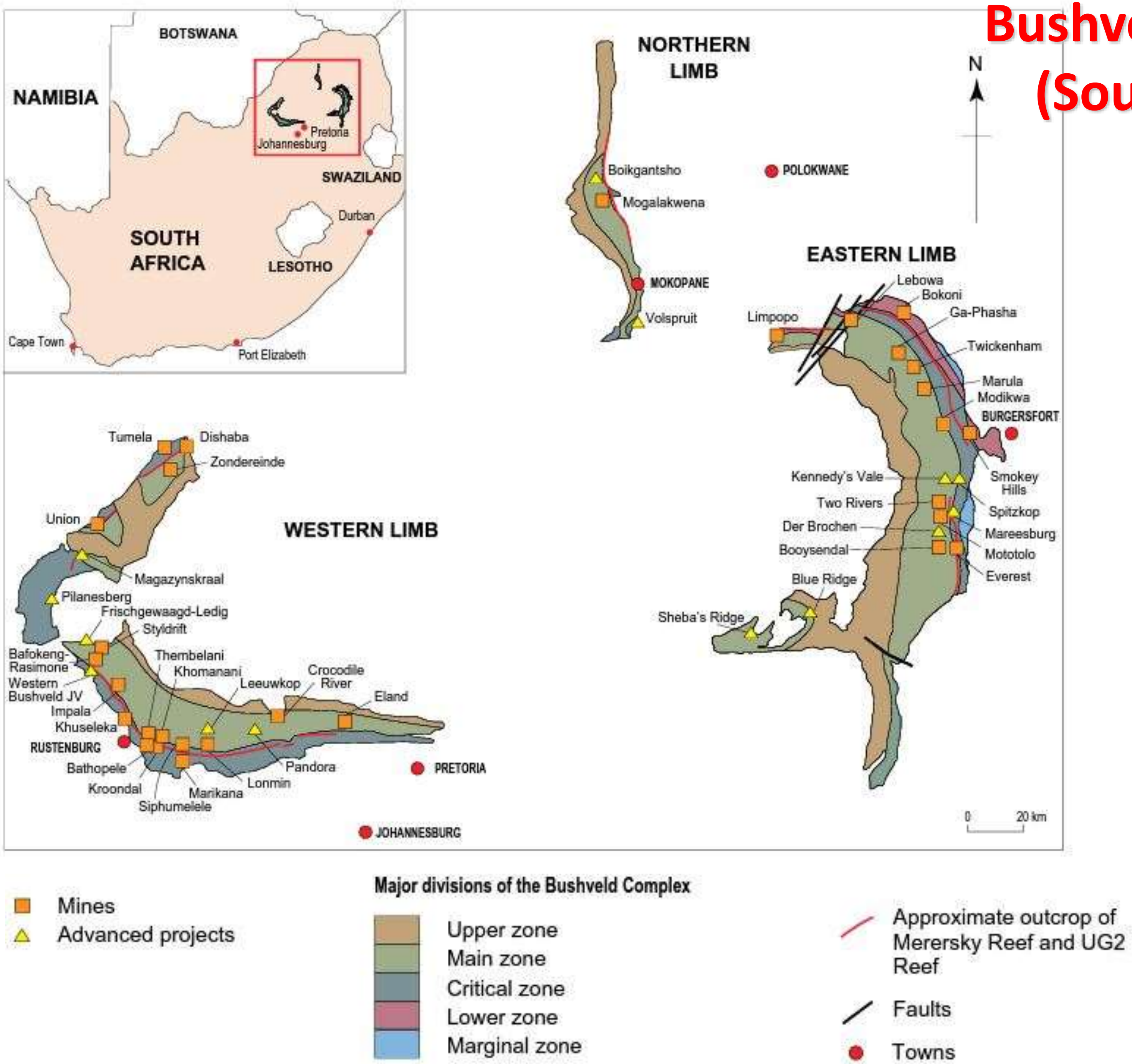
- **Magmatic PGM deposits**, found in mafic and ultramafic igneous rocks, are of two principal types:

  1) **PGM-dominant deposits** which are associated with **sparse, dispersed sulfide mineralization**. Four classes of PGM-dominant deposits are recognized:

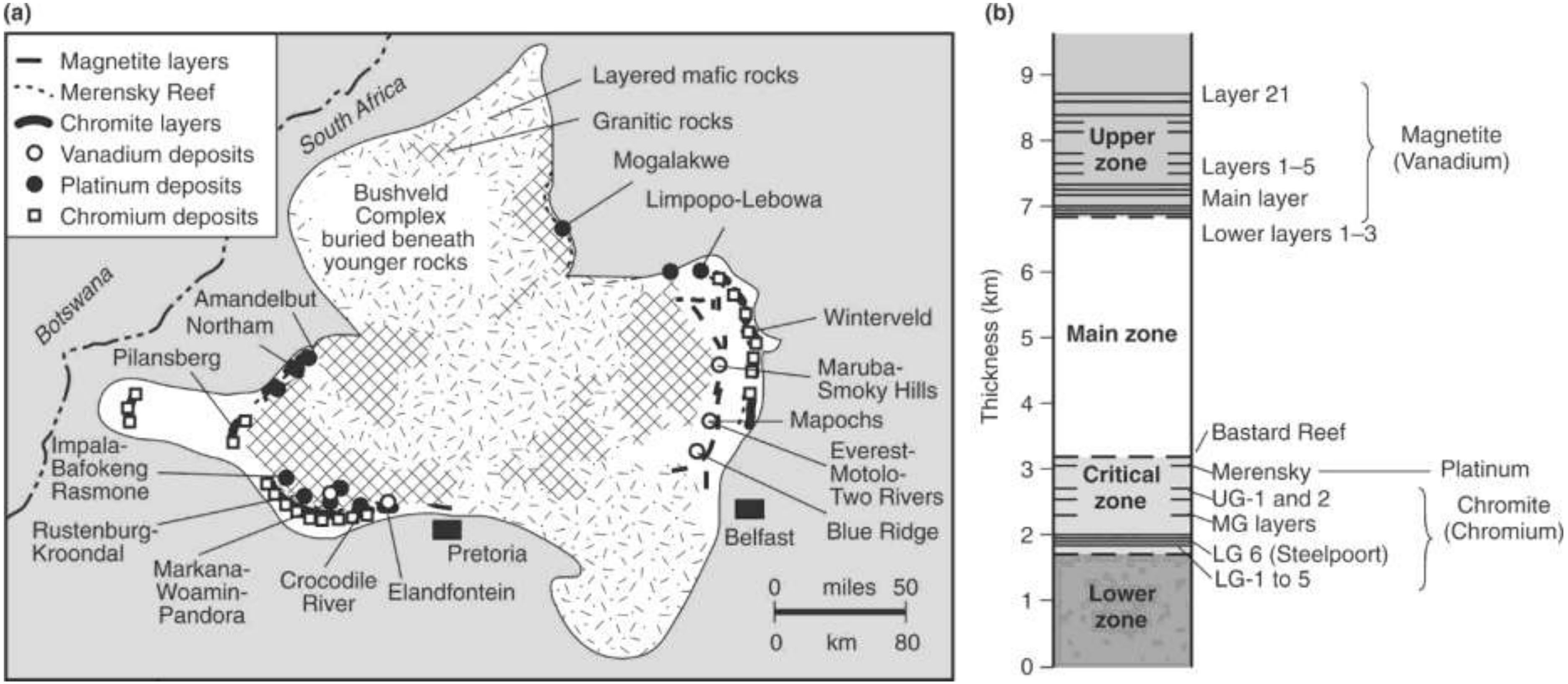
     - **Merensky Reef type**;
     - **Chromitite reef type**;
     - **Contact type**;
     - **Dunite pipes**.

  2) **Ni-Cu sulfide deposits** in which the PGM occur in association with **sulfide-rich ores**. In simple terms PGM-sulfide deposits are derived from magmatic processes of **crystallization**, **differentiation** and **concentration**. The magma becomes **saturated with S** and an **immiscible sulfide liquid** separates from the magma as disseminated droplets. On account of their **chalcophile behavior the PGM** are concentrated **strongly in the sulfide liquid** and are, therefore, scavenged from the silicate liquid.

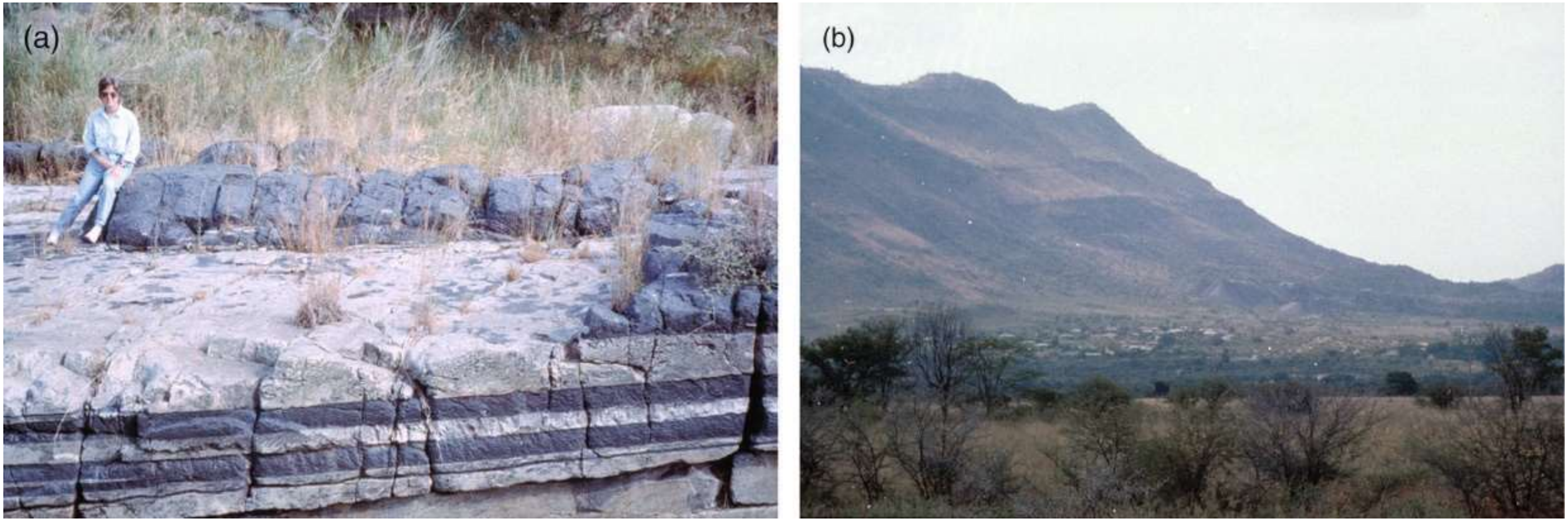
Bushveld complex (South Africa)



Bushveld complex (South Africa)

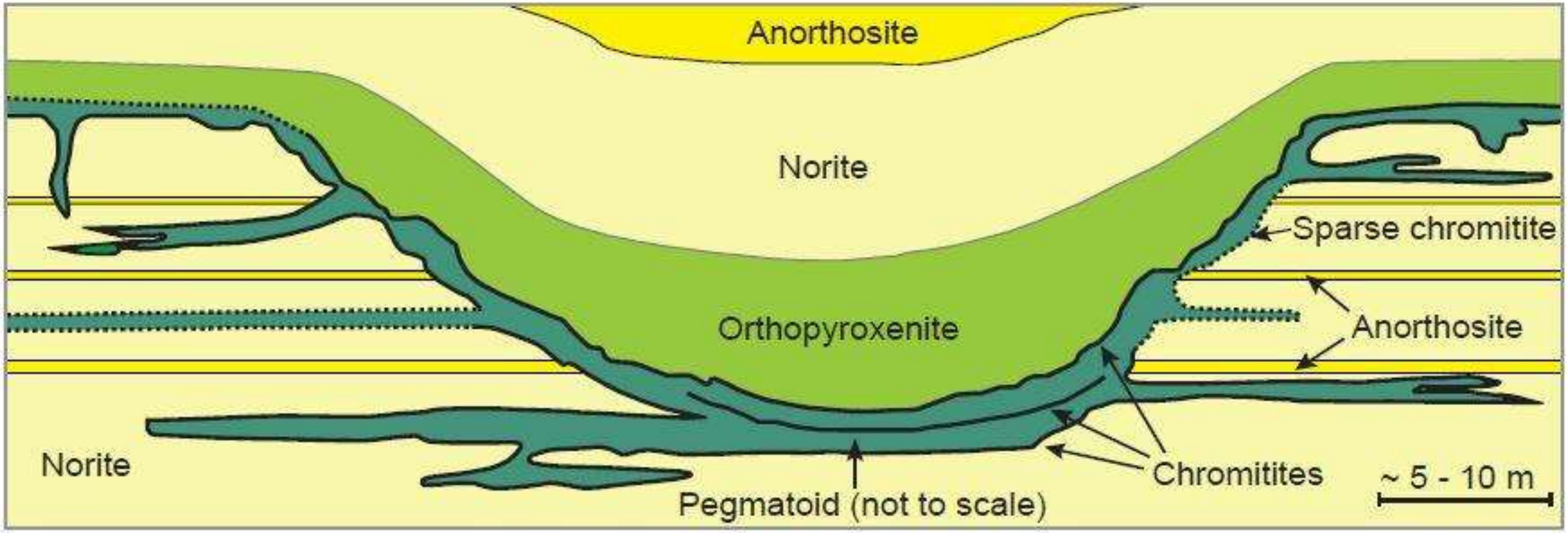


Bushveld complex (South Africa)



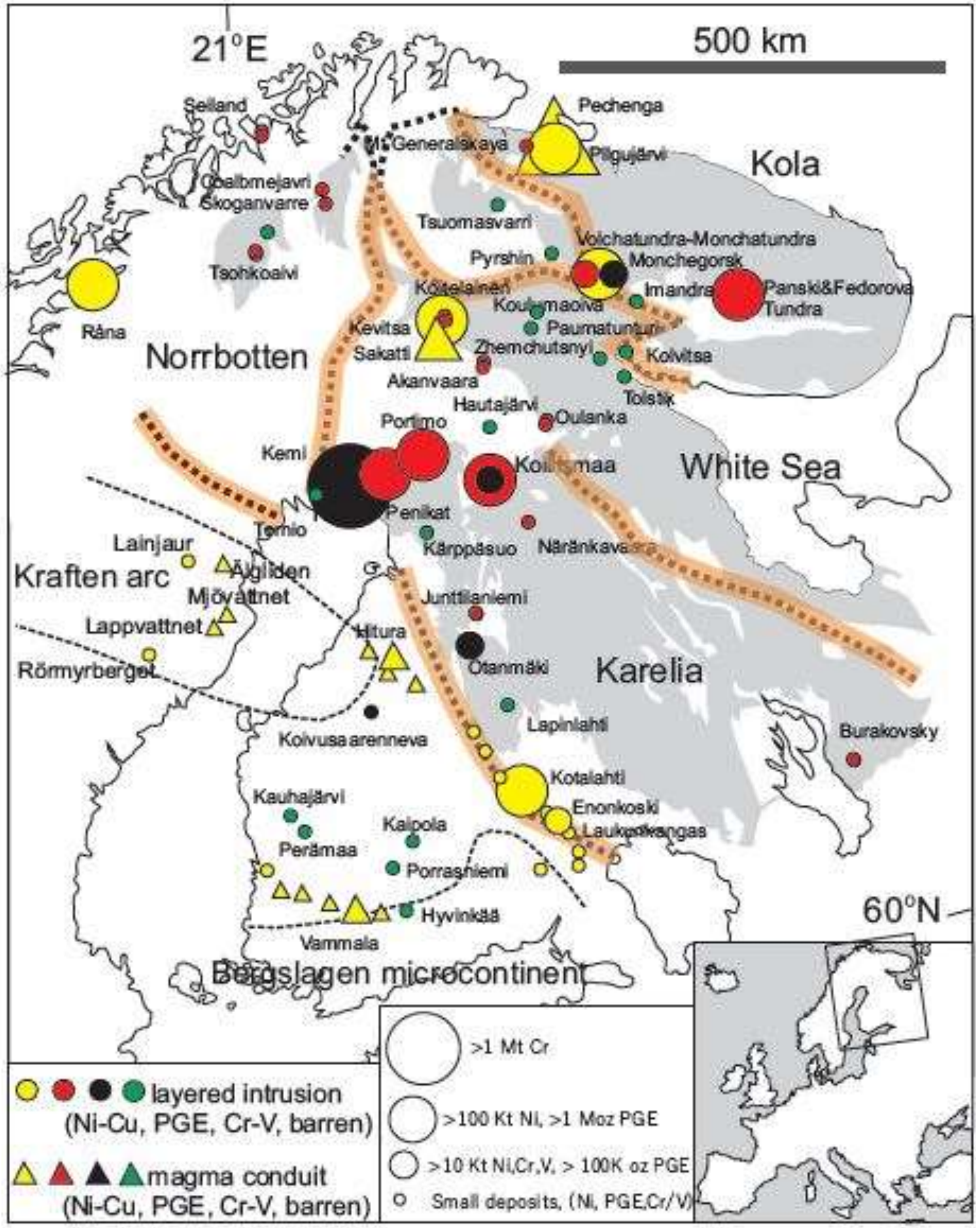
Bushveld chromite deposits, eastern Transvaal, South Africa. (a) Chromitite layers (black) at Dwars River. (b) Winterveld chromitite mine showing cumulate layers on hillside dipping downward to left. The mine enters at the base of the hill to the right.

Bushveld complex (South Africa) - potholes



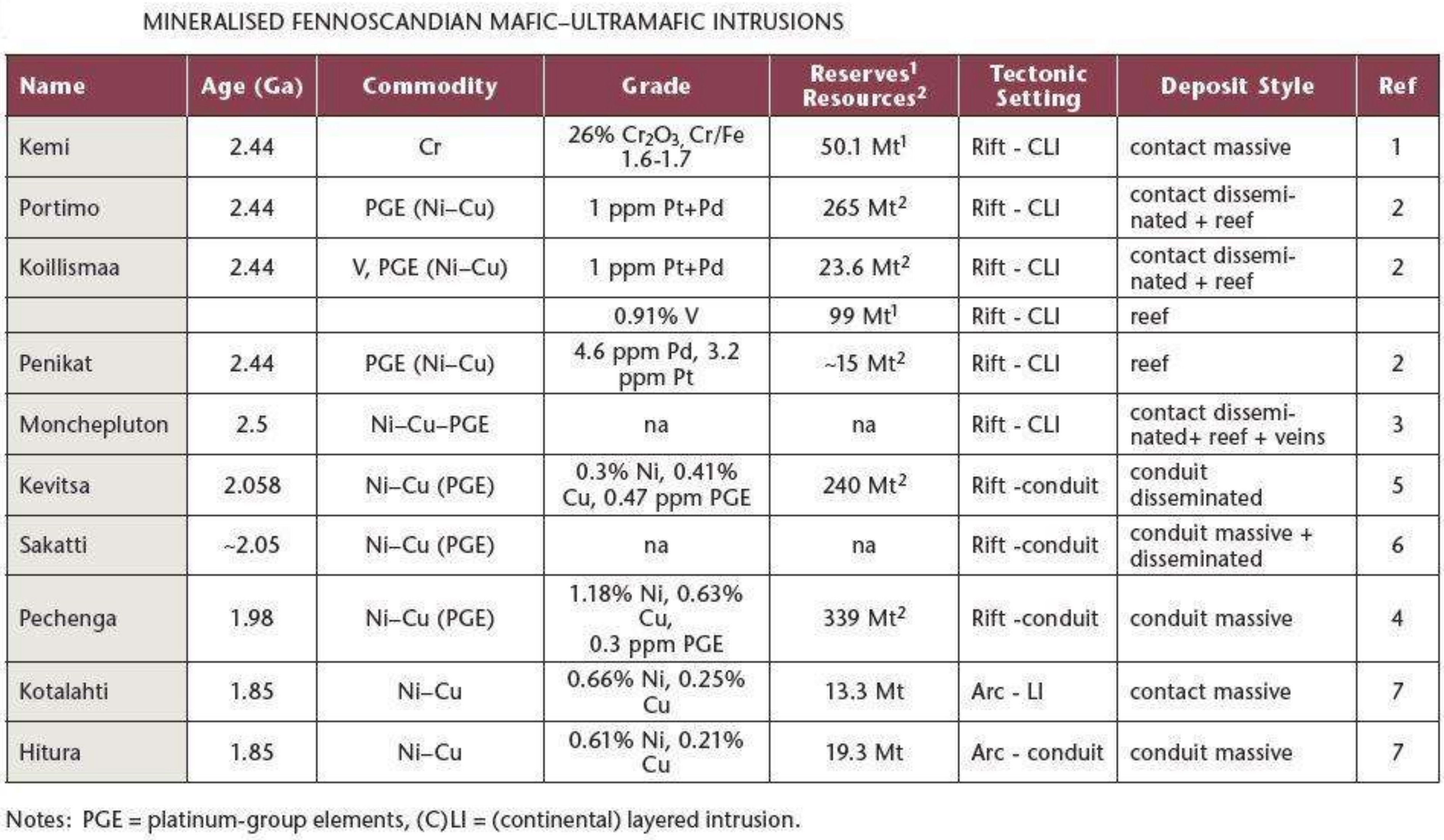
Schematic sketch of a cross section of a pothole filled by Merensky Reef and overlying lithologies in the western Bushveld showing "undercutting" MR, including bounding chromitite seams, extending from the pothole walls into the surrounding layers. MODIFIED FROM LATYPOV ET AL. (2017).

Paleoproterozoic mafic-ultramafic intrusions of Fennoscandia



Precambrian mafic–ultramafic layered intrusions and magmatic feeder conduits of Fennoscandia. Highlighted dashed lines represent craton margins and suture zones. Abbreviation: PGE = platinum-group element(s). Modified after Maier and Groves (2011).

Paleoproterozoic mafic-ultramafic intrusions of Fennoscandia



MINERALISED FENNOSCANDIAN MAFIC–ULTRAMAFIC INTRUSIONS

Name	Age (Ga)	Commodity	Grade	Reserves[1] Resources[2]	Tectonic Setting	Deposit Style	Ref
Kemi	2.44	Cr	26% Cr_2O_3, Cr/Fe 1.6-1.7	50.1 Mt[1]	Rift - CLI	contact massive	1
Portimo	2.44	PGE (Ni–Cu)	1 ppm Pt+Pd	265 Mt[2]	Rift - CLI	contact disseminated + reef	2
Koillismaa	2.44	V, PGE (Ni–Cu)	1 ppm Pt+Pd	23.6 Mt[2]	Rift - CLI	contact disseminated + reef	2
			0.91% V	99 Mt[1]	Rift - CLI	reef	
Penikat	2.44	PGE (Ni–Cu)	4.6 ppm Pd, 3.2 ppm Pt	~15 Mt[2]	Rift - CLI	reef	2
Monchepluton	2.5	Ni–Cu–PGE	na	na	Rift - CLI	contact disseminated+ reef + veins	3
Kevitsa	2.058	Ni–Cu (PGE)	0.3% Ni, 0.41% Cu, 0.47 ppm PGE	240 Mt[2]	Rift -conduit	conduit disseminated	5
Sakatti	~2.05	Ni–Cu (PGE)	na	na	Rift -conduit	conduit massive + disseminated	6
Pechenga	1.98	Ni–Cu (PGE)	1.18% Ni, 0.63% Cu, 0.3 ppm PGE	339 Mt[2]	Rift -conduit	conduit massive	4
Kotalahti	1.85	Ni–Cu	0.66% Ni, 0.25% Cu	13.3 Mt	Arc - LI	contact massive	7
Hitura	1.85	Ni–Cu	0.61% Ni, 0.21% Cu	19.3 Mt	Arc - conduit	conduit massive	7

Notes: PGE = platinum-group elements, (C)LI = (continental) layered intrusion.

Ni-Cu dominant deposits

- **Magmatic Ni-Cu deposits** are the **most important source of Ni worldwide**. **Cu**, **Co** and the **PGM**, mainly **Pd**, are important **by-products**. Au, Ag, Cr, S, Se, Te and Pb are also recovered from some deposits.

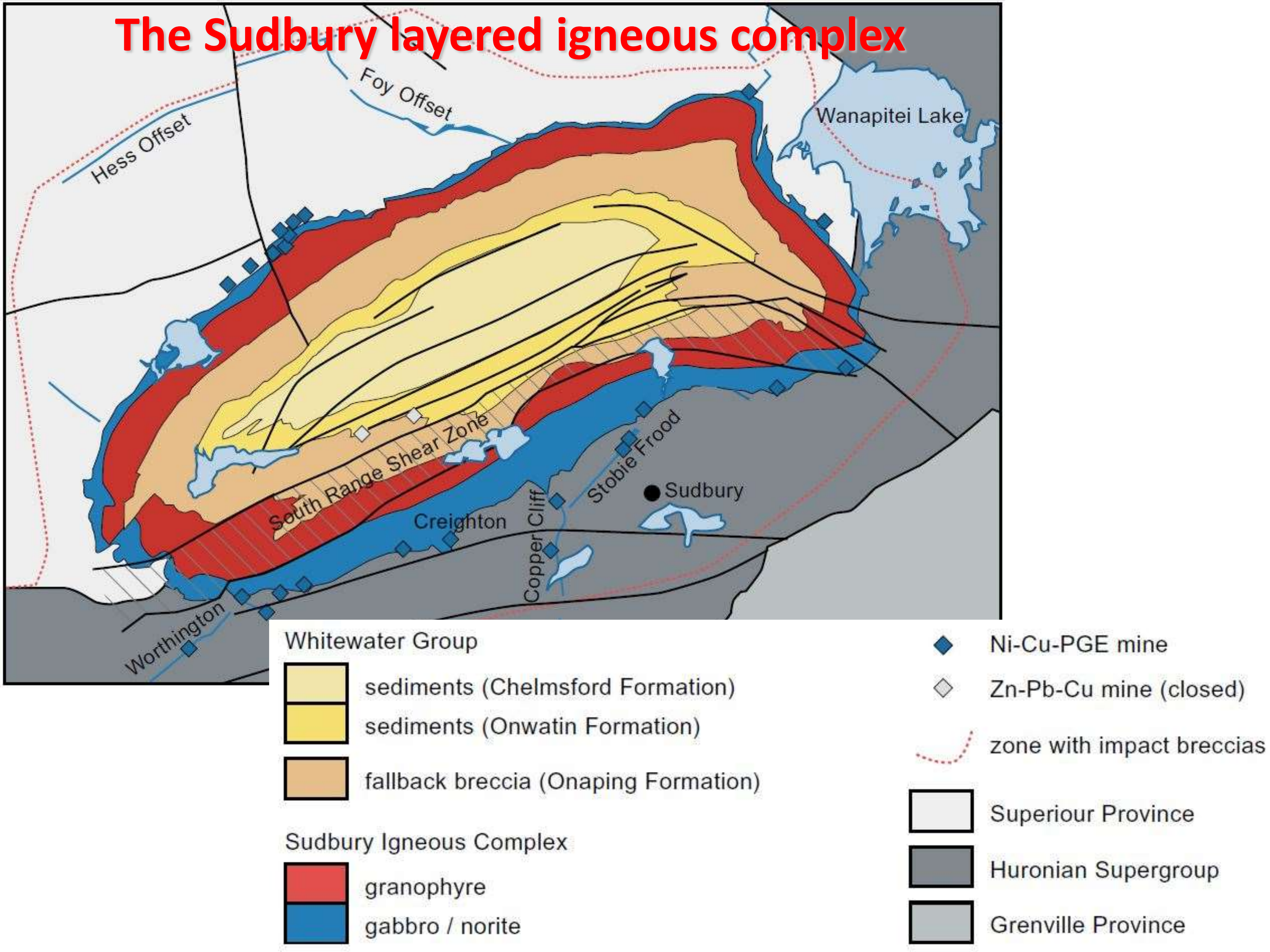
- The dominant ore minerals are **sulfides**, **pyrrhotite**, **pentlandite** and **chalcopyrite**, which generally constitute **more than 10% by volume** of the host rock. **Ni grades** typically range from **0.5 – 3.0% Ni**, with attendant **Cu** in the range **0.2 – 2.0%**. **PGM** contents vary widely from a few ppb up to, exceptionally, **10 ppm**.

- The **size** of the deposits ranges from a **few hundred thousand tonnes** of ore up to a **few of tens of million tonnes**.

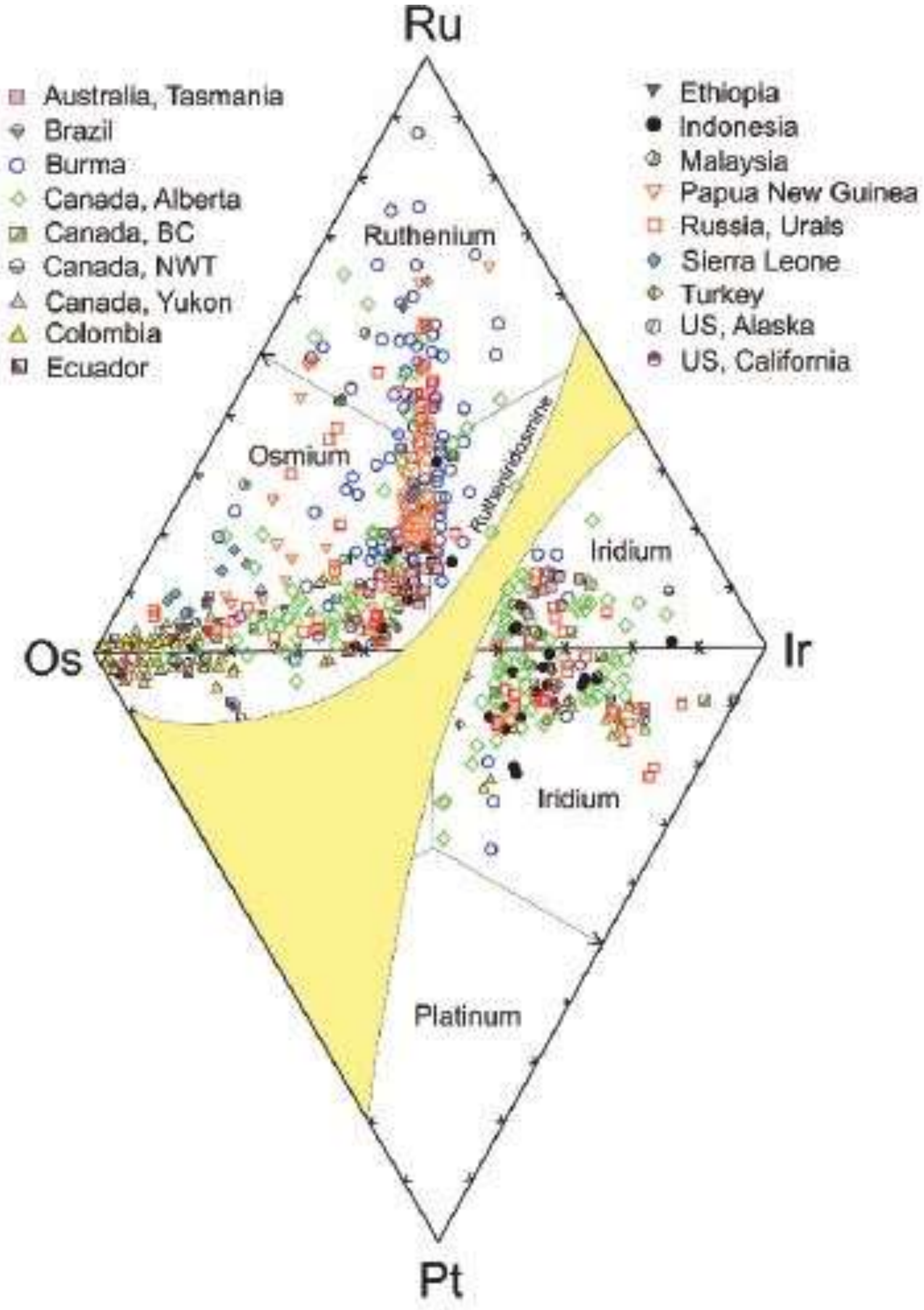
- Magmatic sulfide deposits occur in **diverse geological settings** in rocks ranging in age **from Archean to Permo-Triassic**. Eckstrand and Hulbert (2007) recognized four principal classes:

1. **A meteorite-impact mafic melt** with basal sulfide ores (Sudbury, Canada is the only known example).
2. **Rift- and continental flood basalt**, with associated dykes and sills (Norilsk-Talnakh, Russia; Jinchuan, China).
3. **Komatiitic (Mg-rich) volcanic flows** and related intrusions (Kambalda, Australia; Thompson and Raglan, Canada; Pechenga, NW Russia).
4. Other **mafic - ultramafic intrusions**.

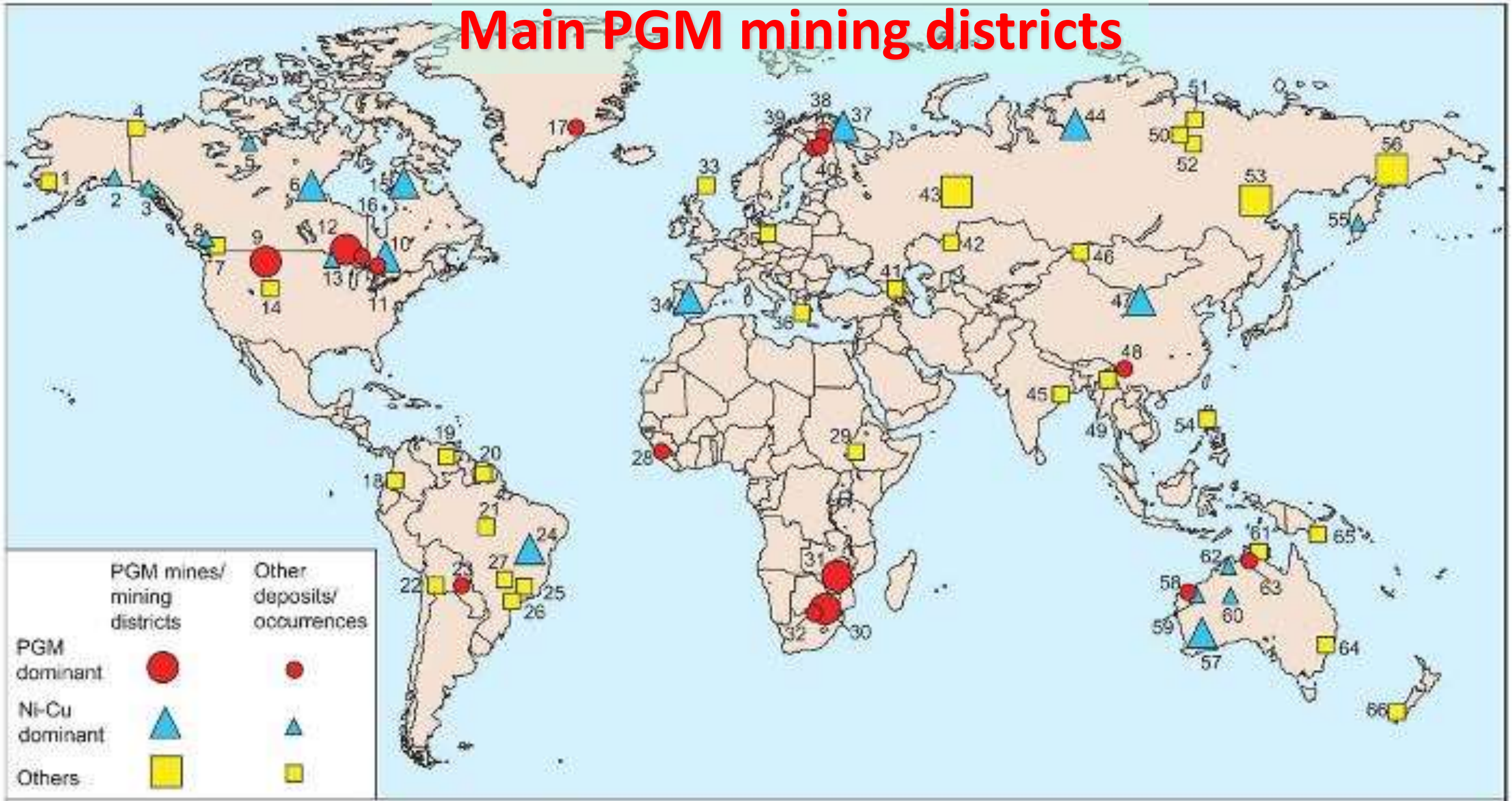
The Sudbury layered igneous complex



Placer deposits



Main PGM mining districts

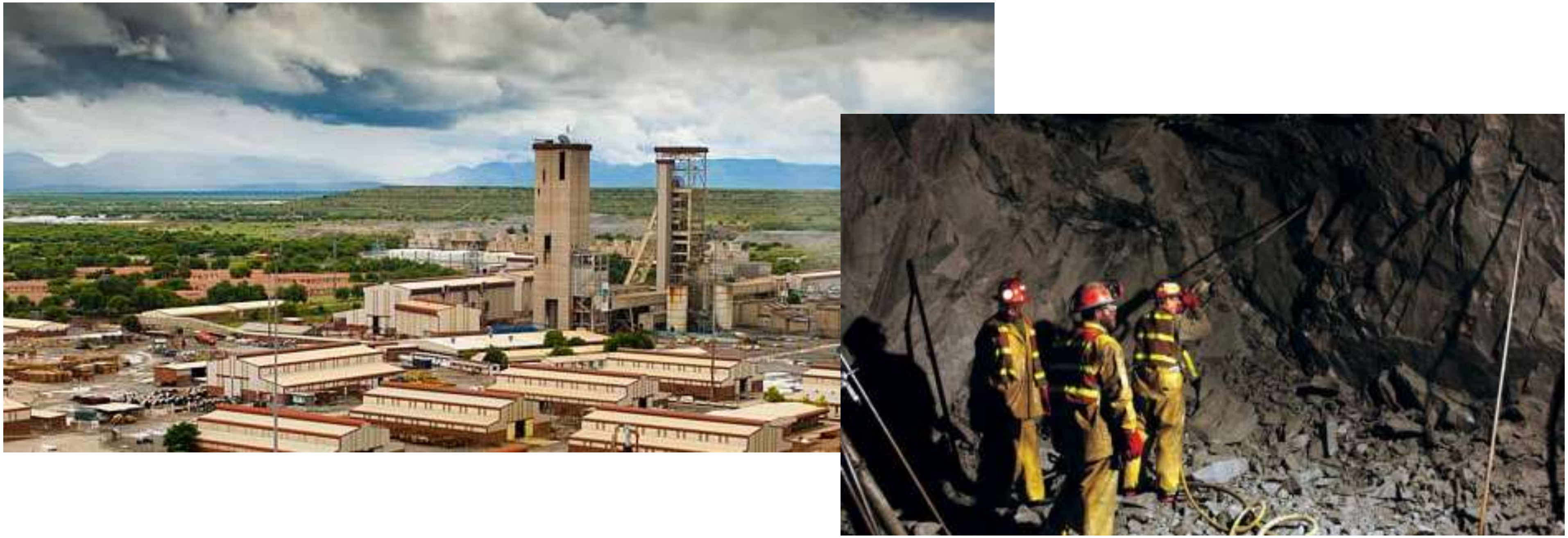


1 Goodnews Bay
2 Wellgreen
3 Nickel Mountain
4 Nick
5 Muskox Intrusion
6 Thompson
7 Tulameen Complex
8 Giant Nickel
9 Stillwater
10 Sudbury
11 East Bull Lake
12 Lac des Iles
13 Duluth
14 New Rambler
15 Ungava
16 Marathon
17 Skaergaard
18 Choco River
19 Cerro La Pinto
20 Platina Creek
21 Serra Pelada
22 Pacajake
23 Rincon del Tigre
24 Jacare
25 Caue
26 Ipanema
27 Catalao
28 Freetown
29 Yubdo
30 Bushveld Complex
31 Great Dyke
32 Stella Intrusion
33 Unst
34 Agua Blanca
35 Kupferschiefer
36 Skouries
37 Pechenga District
38 Keivitsa
39 Penikat
40 Portimo
41 Kadzharan
42 Kempirsai
43 Urals
44 Norilsk-Talnakh
45 Nuasahi
46 Ojut Tolgoi
47 Jinchuan
48 Dali
49 Chindwin Basin
50 Sukhoi Log
51 Inagli
52 Udokan
53 Kondyor
54 Zambales
55 Kvinum
56 Koryak-Kamchatka
57 Eastern Goldfields
58 Munni Munni
59 Radio Hill
60 Nebo-Babel
61 Coronation Hill
62 Sally Malay
63 Panton
64 Fifield
65 Aikora River
66 Southland

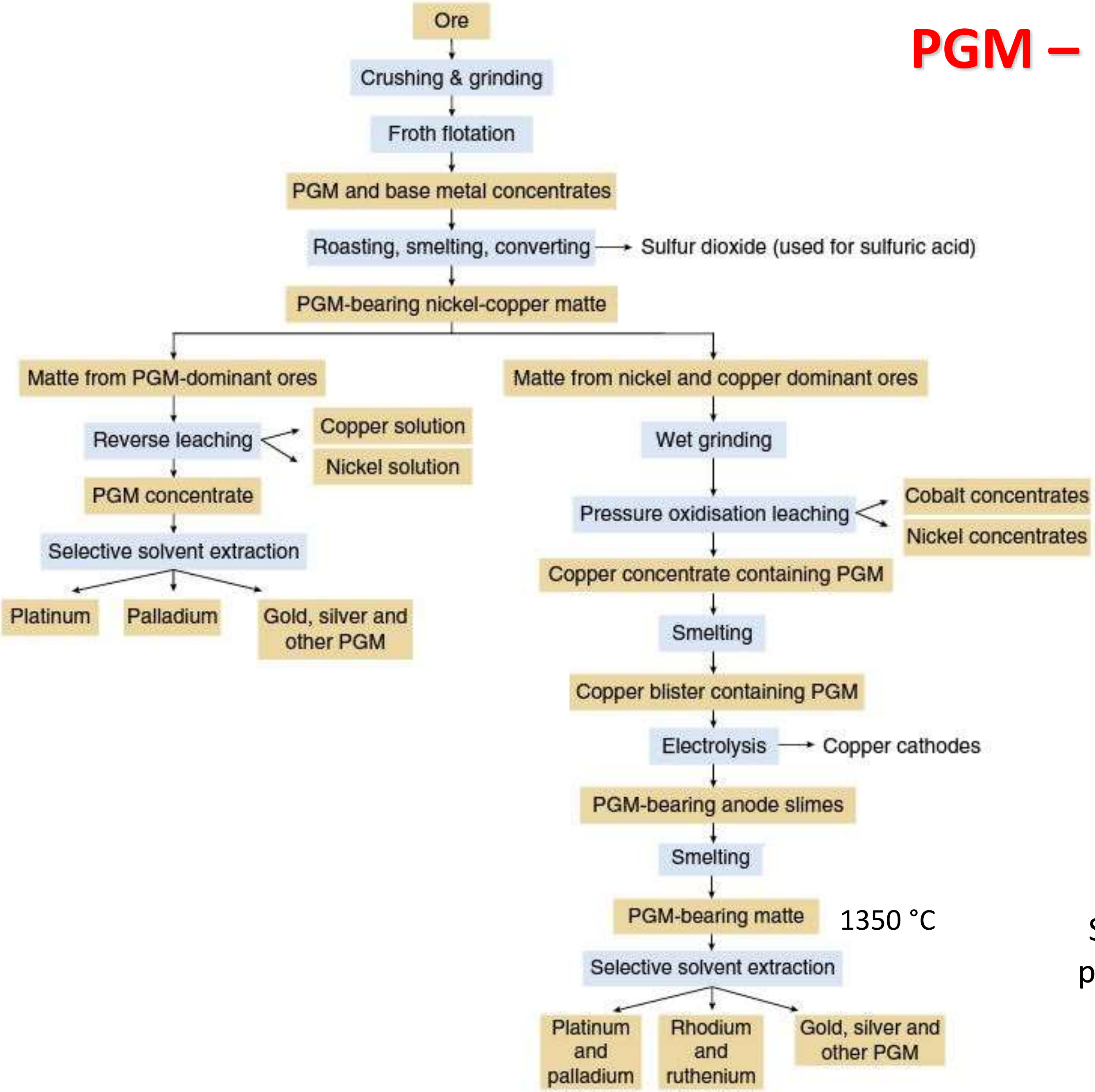
PGM – extraction methods and processing

- **Extraction methods**: dependent on size, morphology, grade and value of by-products. The deepest currently operating mine is Zondereinde (*Northam Platinum Ltd*, W limb of the Bushveld Complex), where mining takes place at a maximum depth of 2.2 km (“hydropower”, water at 5 °C).

- **Processing**: crushing the ore and separating PGM-bearing and gangue minerals, using a range of physical and chemical processes. Different procedures are used for processing **sulfide-poor ore** (e.g. Merensky and UG2) and **sulfide-dominant ores** (e.g. Norilsk) due to their contrasting chemical, mineralogical and physical properties.



PGM – processing


Ore
Crushing & grinding
Froth flotation
PGM and base metal concentrates
Roasting, smelting, converting → Sulfur dioxide (used for sulfuric acid)
PGM-bearing nickel-copper matte

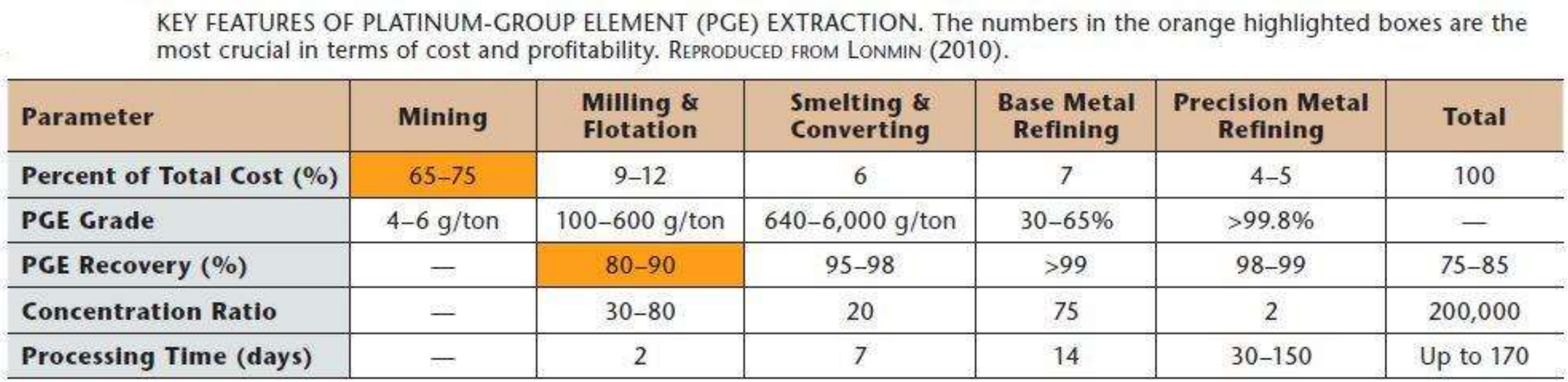
Matte from PGM-dominant ores
Reverse leaching → Copper solution, Nickel solution
PGM concentrate
Selective solvent extraction
Platinum
Palladium
Gold, silver and other PGM

Matte from nickel and copper dominant ores
Wet grinding
Pressure oxidisation leaching → Cobalt concentrates, Nickel concentrates
Copper concentrate containing PGM
Smelting
Copper blister containing PGM
Electrolysis → Copper cathodes
PGM-bearing anode slimes
Smelting
PGM-bearing matte
1350 °C
Selective solvent extraction
Platinum and palladium
Rhodium and ruthenium
Gold, silver and other PGM

Schematic flowsheet for the processing of PGM-dominant and nickel–copper-dominant ores.

Schematic flowsheet for the processing of **PGM-dominant** and **Ni-Cu dominant ores**.

PGM – extraction methods and processing



KEY FEATURES OF PLATINUM-GROUP ELEMENT (PGE) EXTRACTION. The numbers in the orange highlighted boxes are the most crucial in terms of cost and profitability. Reproduced from Lonmin (2010).

Parameter	Mining	Milling & Flotation	Smelting & Converting	Base Metal Refining	Precision Metal Refining	Total
Percent of Total Cost (%)	65–75	9–12	6	7	4–5	100
PGE Grade	4–6 g/ton	100–600 g/ton	640–6,000 g/ton	30–65%	>99.8%	—
PGE Recovery (%)	—	80–90	95–98	>99	98–99	75–85
Concentration Ratio	—	30–80	20	75	2	200,000
Processing Time (days)	—	2	7	14	30–150	Up to 170

Pt and Pd – specifications and uses

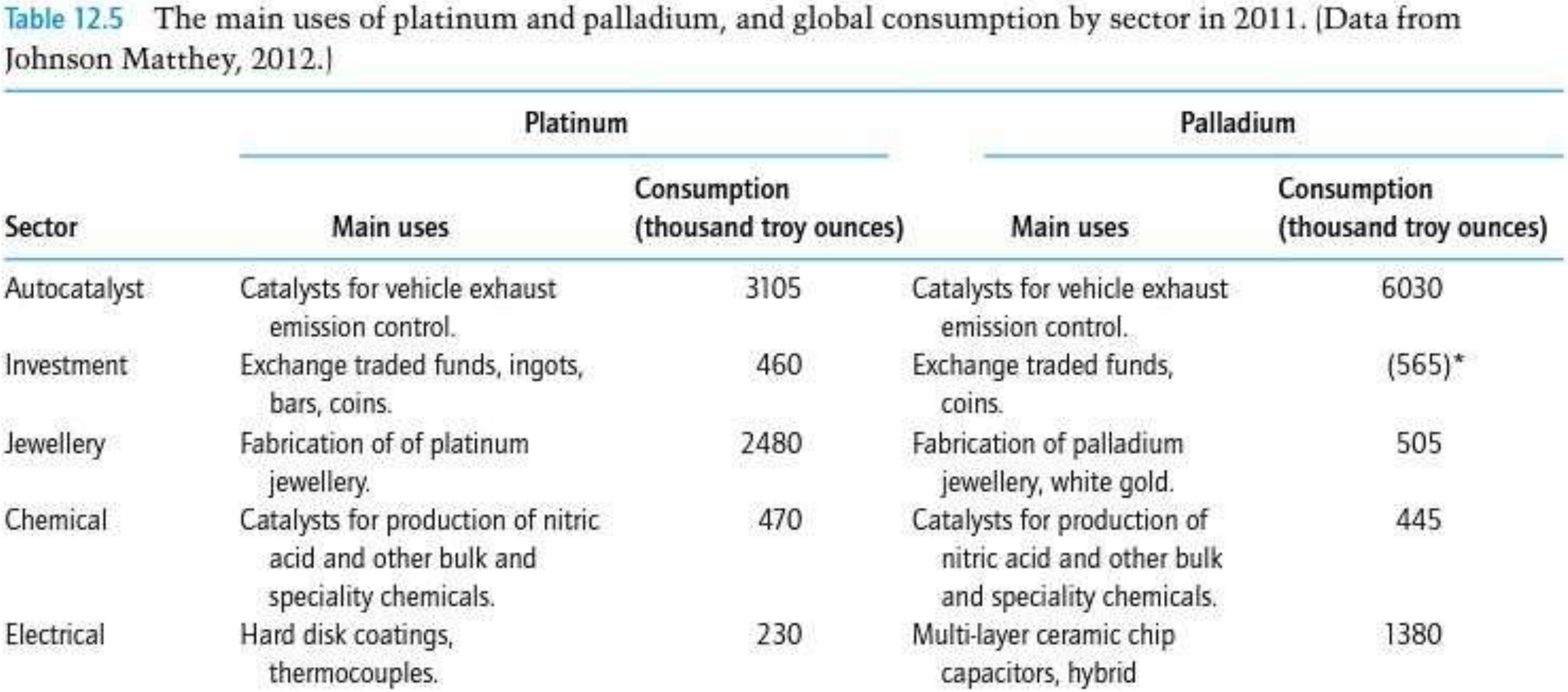
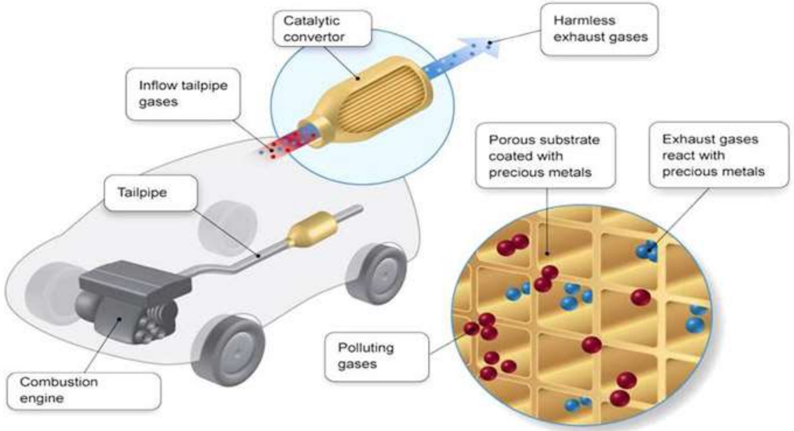
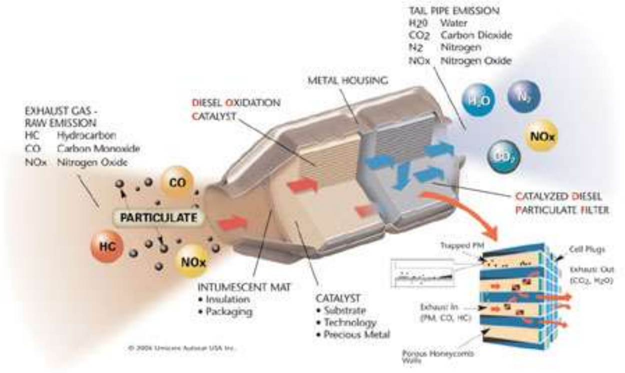


Table 12.5 The main uses of platinum and palladium, and global consumption by sector in 2011. (Data from Johnson Matthey, 2012.)

	Platinum		Palladium	
Sector	Main uses	Consumption (thousand troy ounces)	Main uses	Consumption (thousand troy ounces)
Autocatalyst	Catalysts for vehicle exhaust emission control.	3105	Catalysts for vehicle exhaust emission control.	6030
Investment	Exchange traded funds, ingots, bars, coins.	460	Exchange traded funds, coins.	(565)*
Jewellery	Fabrication of of platinum jewellery.	2480	Fabrication of palladium jewellery, white gold.	505
Chemical	Catalysts for production of nitric acid and other bulk and speciality chemicals.	470	Catalysts for production of nitric acid and other bulk and speciality chemicals.	445
Electrical	Hard disk coatings, thermocouples.	230	Multi-layer ceramic chip capacitors, hybrid	1380





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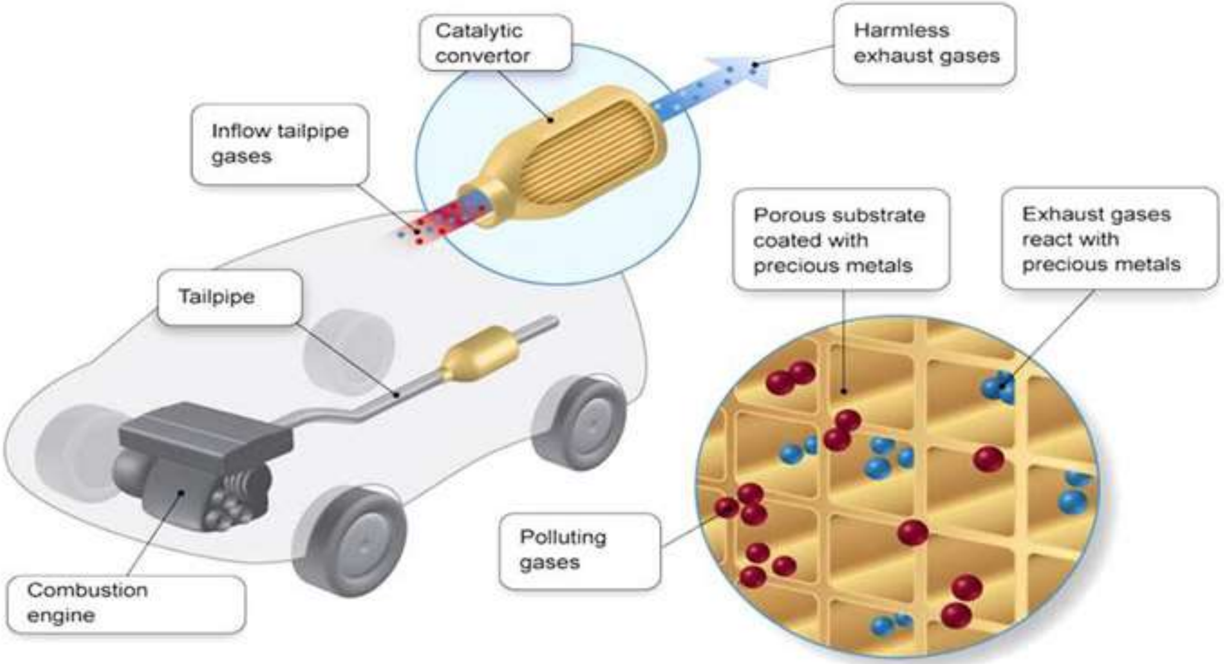
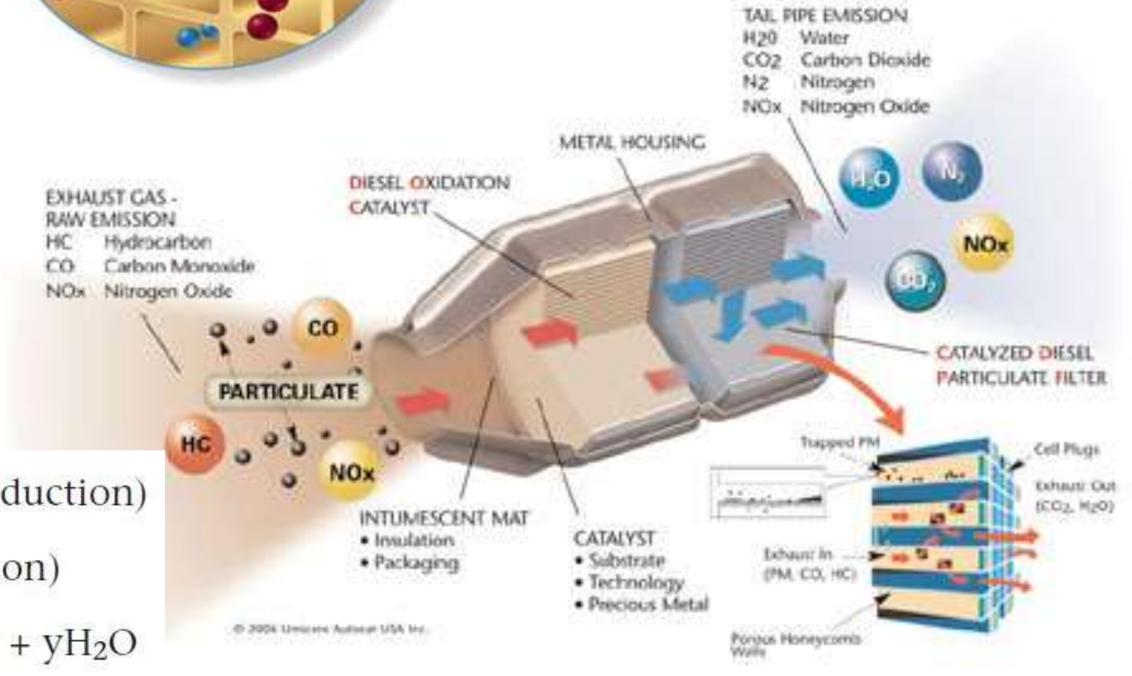
Pt and Pd – specifications and uses





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(1) $2NOx = 1/2\ N_2 + xO_2$ (NOx reduction)

(2) $2CO + O_2 = 2CO_2$ (CO oxidation)

(3) $2C_xH_y + (2x+y/2)O_2 \rightarrow 2xCO_2 + yH_2O$ (oxidation of unburned fuel)

Pt and Pd – specifications and uses

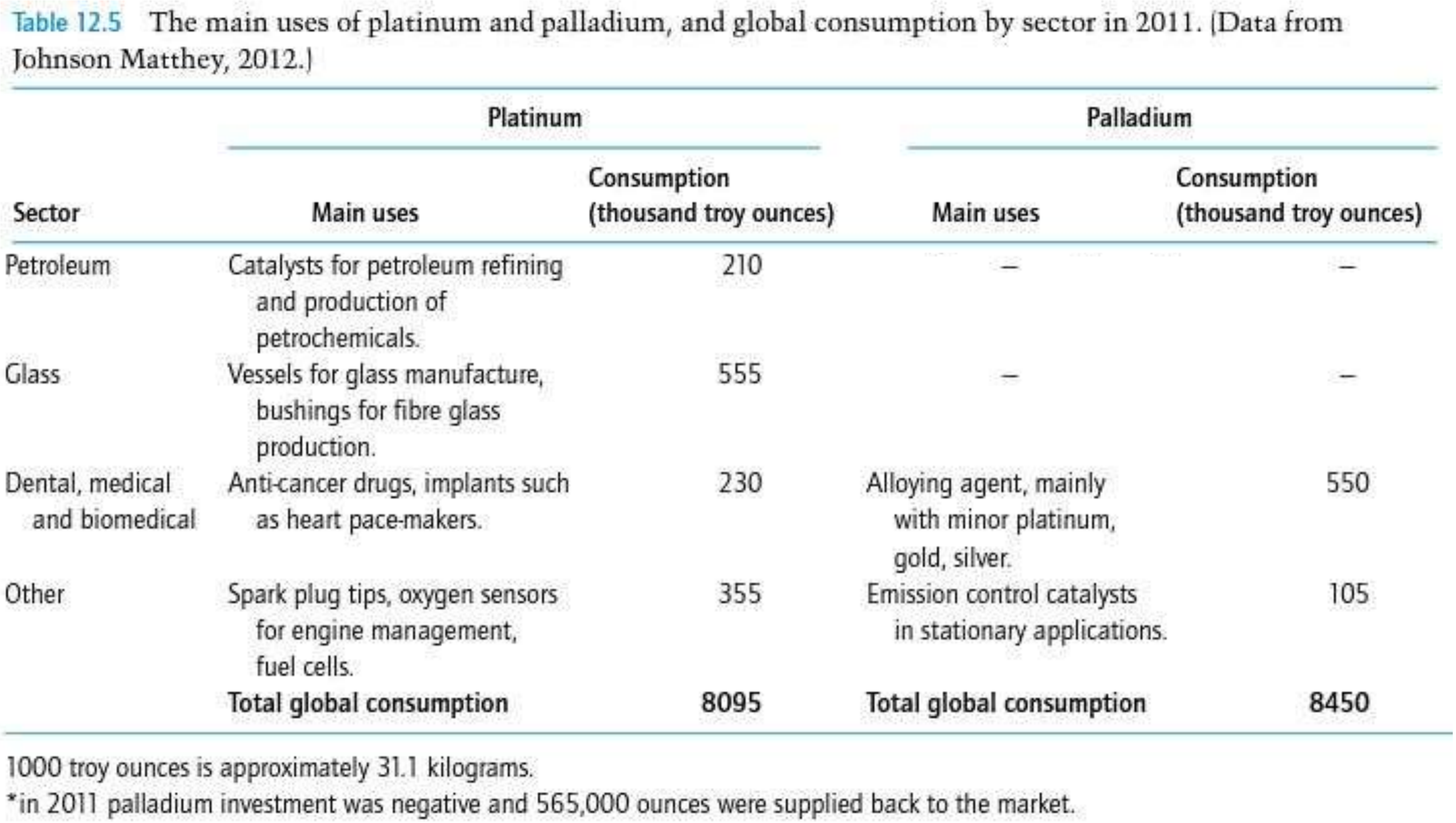


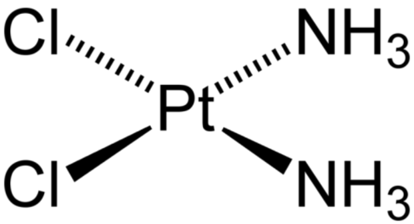
Table 12.5 The main uses of platinum and palladium, and global consumption by sector in 2011. (Data from Johnson Matthey, 2012.)

	Platinum		Palladium	
Sector	Main uses	Consumption (thousand troy ounces)	Main uses	Consumption (thousand troy ounces)
Petroleum	Catalysts for petroleum refining and production of petrochemicals.	210	–	–
Glass	Vessels for glass manufacture, bushings for fibre glass production.	555	–	–
Dental, medical and biomedical	Anti-cancer drugs, implants such as heart pace-makers.	230	Alloying agent, mainly with minor platinum, gold, silver.	550
Other	Spark plug tips, oxygen sensors for engine management, fuel cells.	355	Emission control catalysts in stationary applications.	105
	Total global consumption	**8095**	**Total global consumption**	**8450**

1000 troy ounces is approximately 31.1 kilograms.

*in 2011 palladium investment was negative and 565,000 ounces were supplied back to the market.

PGM – uses



Pt or Pt-Ir through wires for multi-pin hermetic seal, inside the seal housing (0.015″ (0.381 mm) and 0.013″ (0.330 mm))

Pt-Ir, MP35N® or stainless steel machined parts for terminal connector

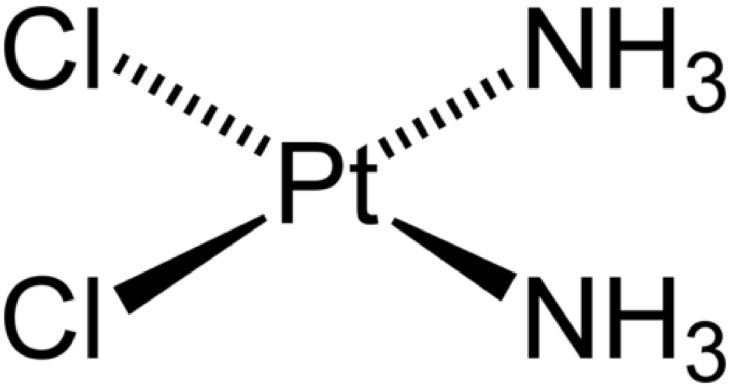
Pt or Pt-Ir wire and ribbon multifilar coils for high-voltage shocking electrodes

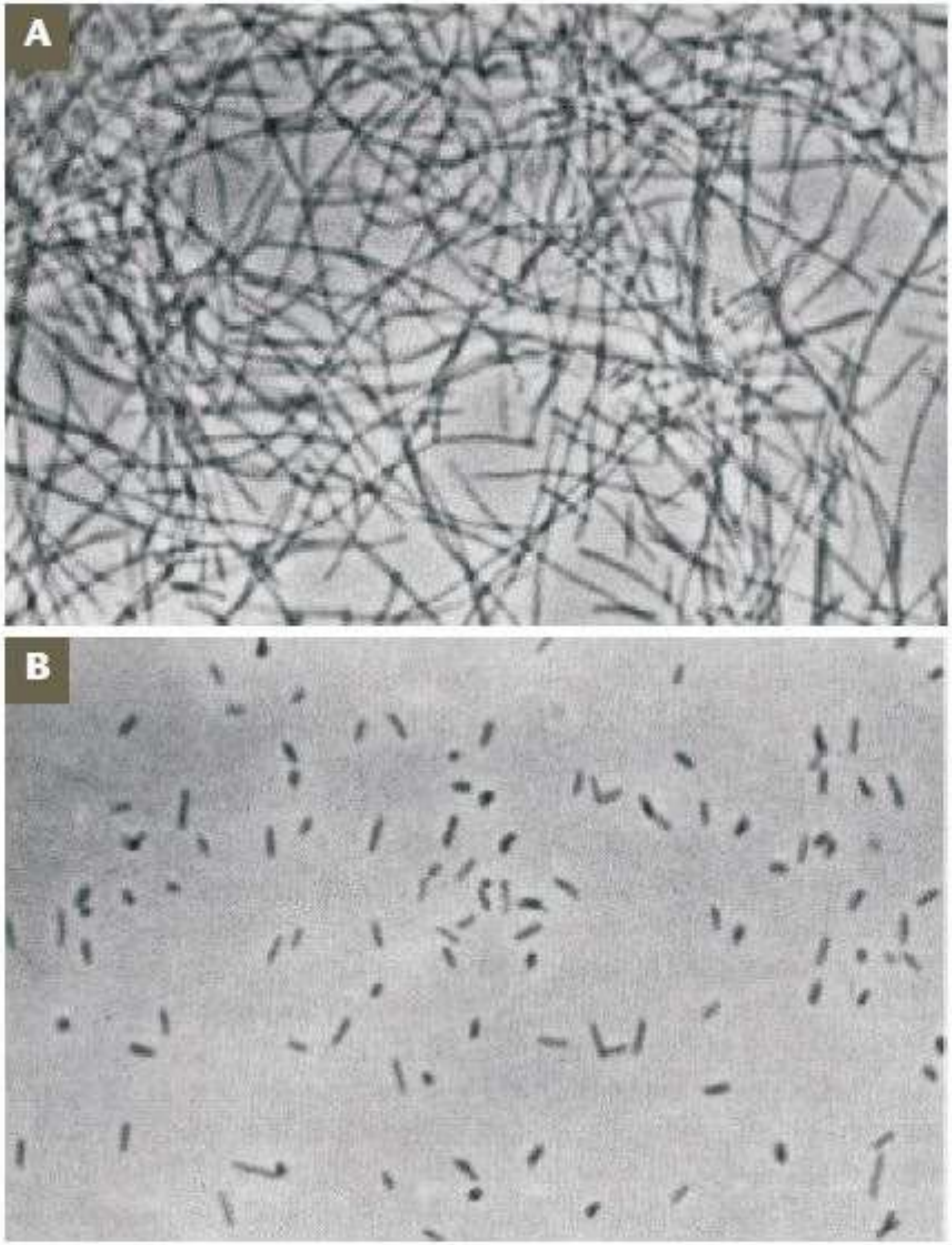
Pt-Ir alloy rings for shocking electrodes

TiNi-coated Pt-Ir machined parts for passive fixation leads

Porous TiNi-coated Pt-Ir helix and post assembly for active fixation leads

Pt compounds as anti-cancer drugs





Phase contrast photomicrographs of *E. coli* cultured in growth medium containing (**A**) 8 ppm of platinum as the neutral species $[PtCl_4\text{-}(NH_3)_2]^0$ and (**B**) less than 6 ppm of platinum as the doubly negative species $[PtCl_6]^{2-}$. Magnified 600x. The image in (**A**) shows the development of filamentous forms, in contrast to the normal sausage shape shown in (**B**), indicating the inhibiting effect of $[PtCl_4\text{-}(NH_3)_2]^0$ on cell division, but not on growth. From Rosenberg et al. (1967). COPYRIGHT 1967 BY THE AMERICAN SOCIETY FOR BIOCHEMISTRY AND MOLECULAR BIOLOGY. USED WITH PERMISSION OF AMERICAN SOCIETY FOR BIOCHEMISTRY AND MOLECULAR BIOLOGY IN THE FORMAT MAGAZINE VIA COPYRIGHT CLEARANCE CENTER

Pt and Pd – main applications

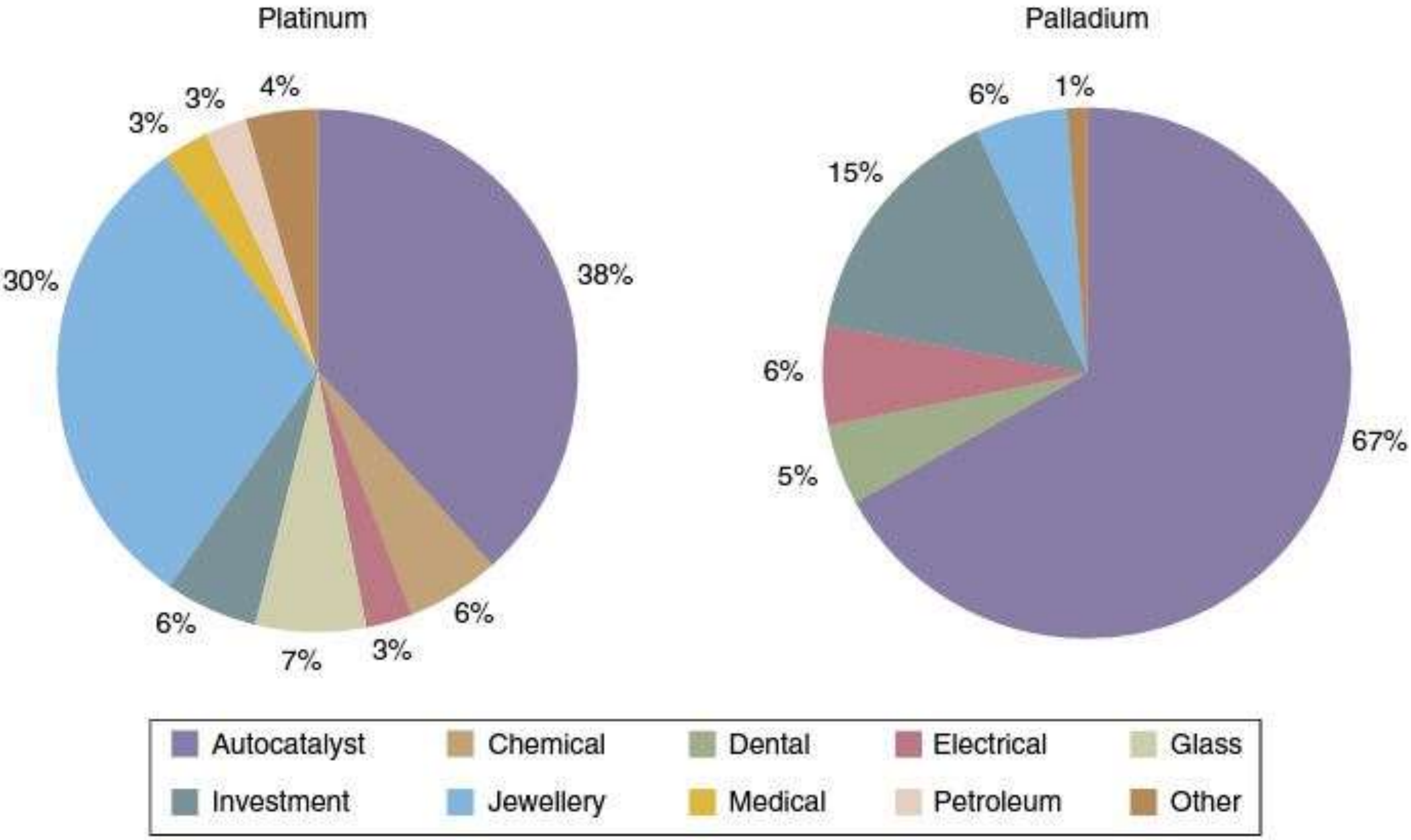


Figure 12.4 The main applications of platinum and palladium in 2011. (Data from Johnson Matthey, 2012.)

PGM – recycling and substitution

Recycling

- The durability of PGM in use, combined with their high prices, has ensured a growing interest in using them efficiently and recycling them whenever possible. For Pt, approximately 23% is derived from recycling, 19% for Pd and 27% for Rh. The largest contributions come from **autocatalysts**, **jewellery** and **electronic scrap**. High recycling rates are also achieved in the manufacture of **chemicals** and **oil refining**, where the **spent catalysts** are returned directly to a recycling company.

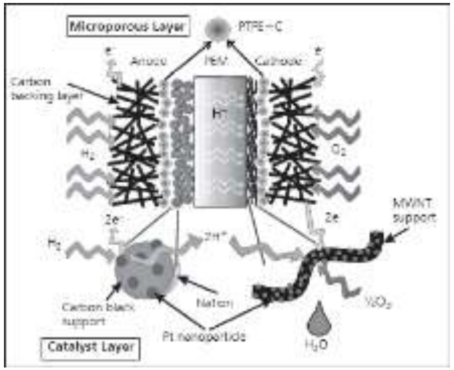
- Medical and biomedical uses, spark plugs, sensors and hard disks are dissipated.

Substitution

- In many applications one PGM can substitute for another (e.g. Pt and Pd in autocatalysts)

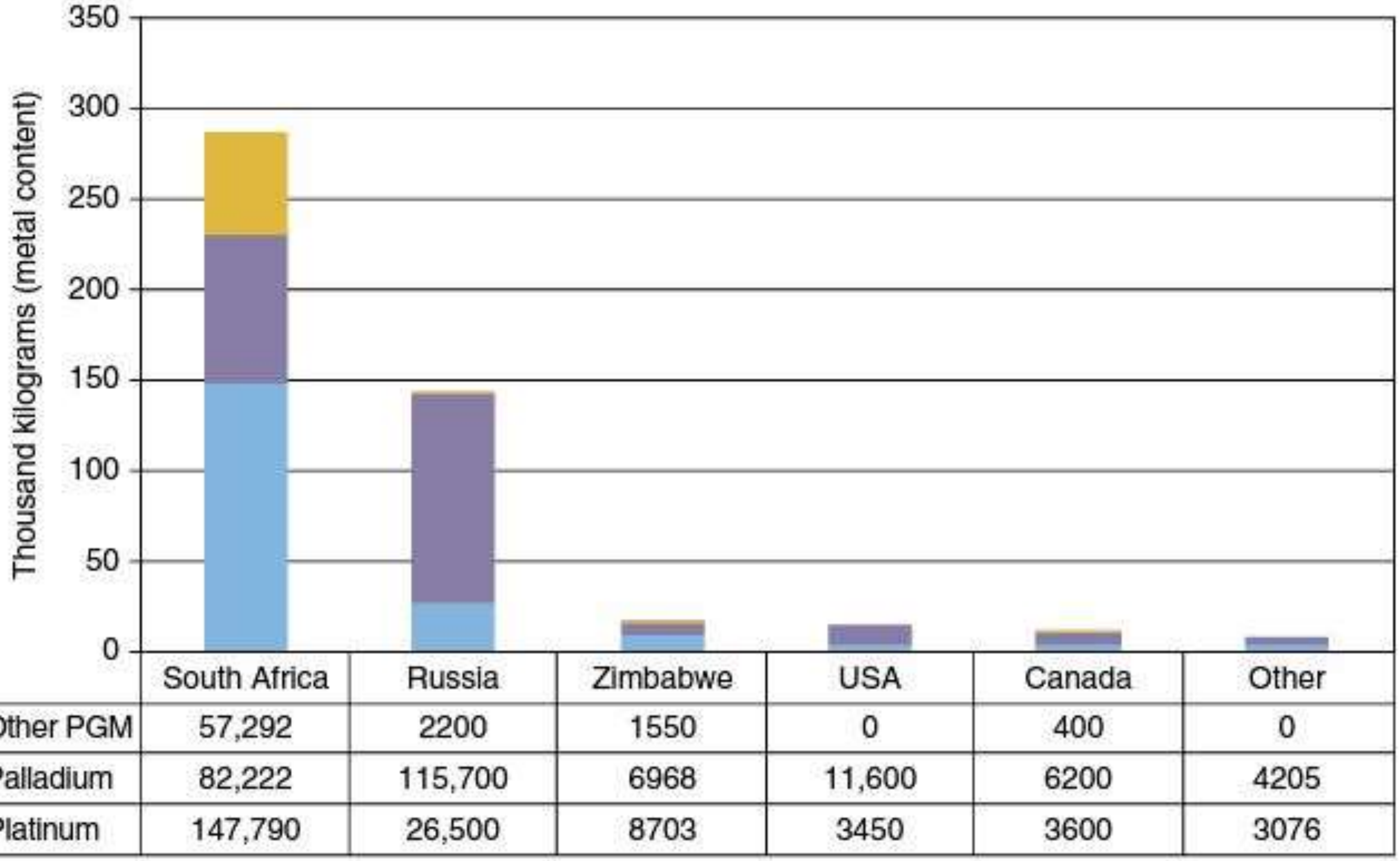
- **Electronic applications:** Ni and Cu (reduction in performance).

- There is considerable interest in **reducing the amount of PGM** used in **fuel cells**.



PGM – resources and reserves

- The **Merensky**, **UG2** and **Platreef** in **South Africa** dominate world PGM resources (> 250M oz t, 800M oz t?). Proven and probable ore reserves in the **Norilsk-Talnakh** area (Russia) are about 55M oz tof Pd and 13M troy ounces of Pt.*[1 oz t (troy ounce)=31.103 g].*



	South Africa	Russia	Zimbabwe	USA	Canada	Other
🟨 Other PGM	57,292	2200	1550	0	400	0
🟪 Palladium	82,222	115,700	6968	11,600	6200	4205
🟦 Platinum	147,790	26,500	8703	3450	3600	3076

Figure 12.6 World mine production of platinum, palladium and other PGM in 2010 by country. (Data from British Geological Survey, 2012.) (1 kilogram equals 32.151 troy ounces.)

PGM – production

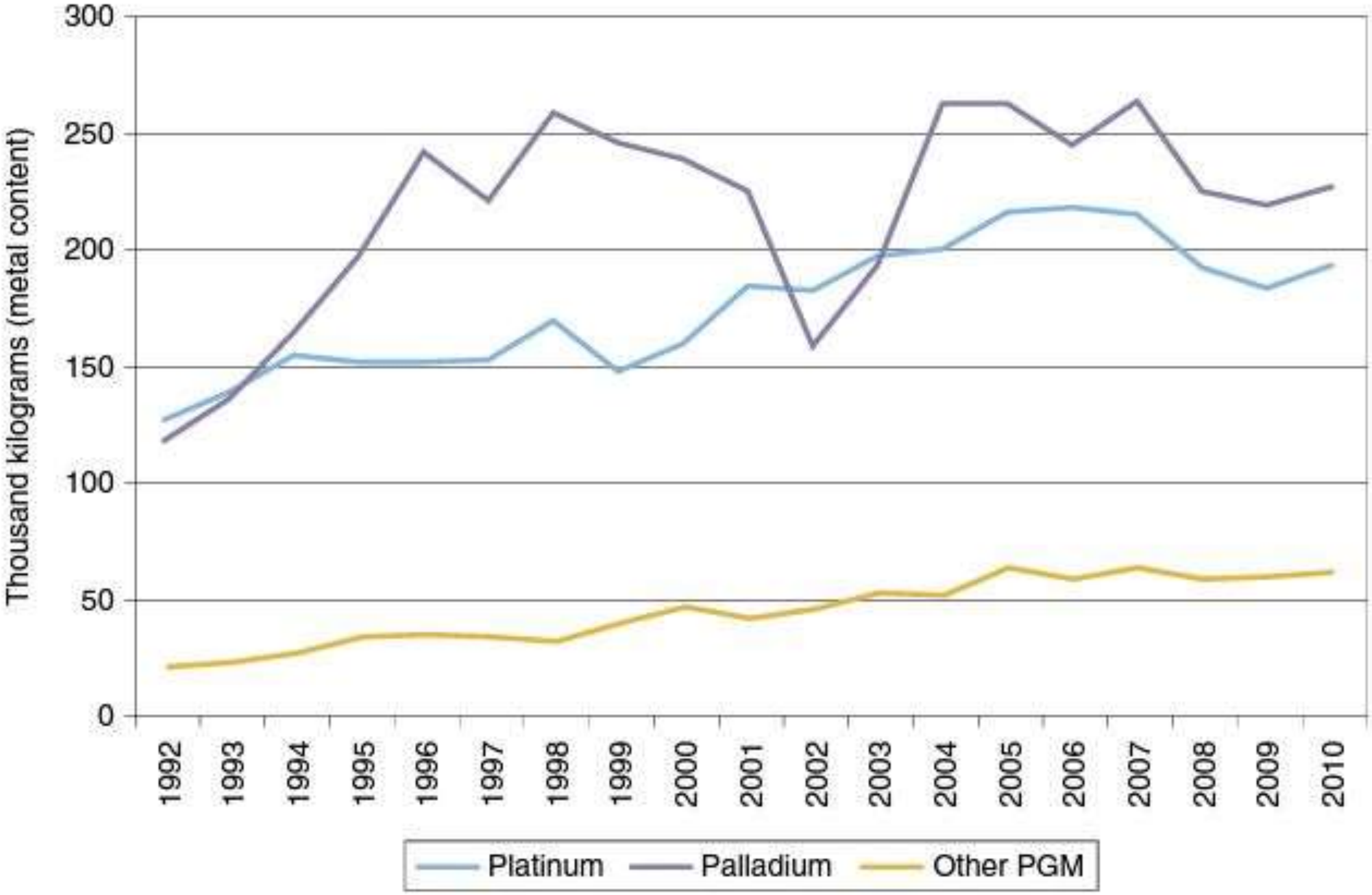


Figure 12.5 World mine production of platinum, palladium and other PGM, 1992–2010. (Data from British Geological Survey World Mineral Statistics database.) (1 kilogram equals 32.151 troy ounces.)

PGM – main exporters

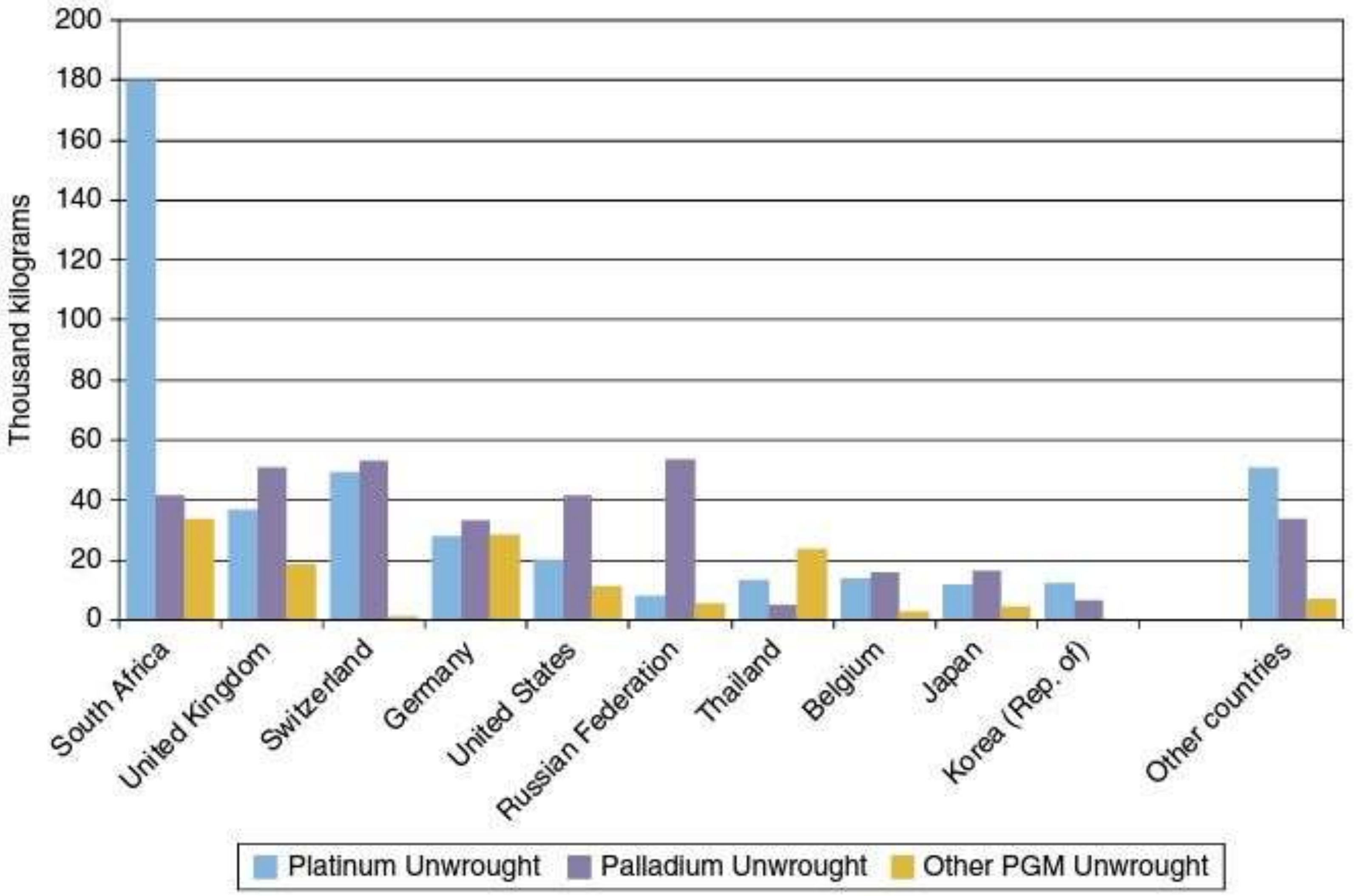


Figure 12.8 Major exporters of platinum metal, concentrates and intermediate products, 2009. (Data from British Geological Survey World Mineral Statistics database and UN Comtrade, 2013.) (1 kilogram equals 32.151 troy ounces.)

PGM – major importers

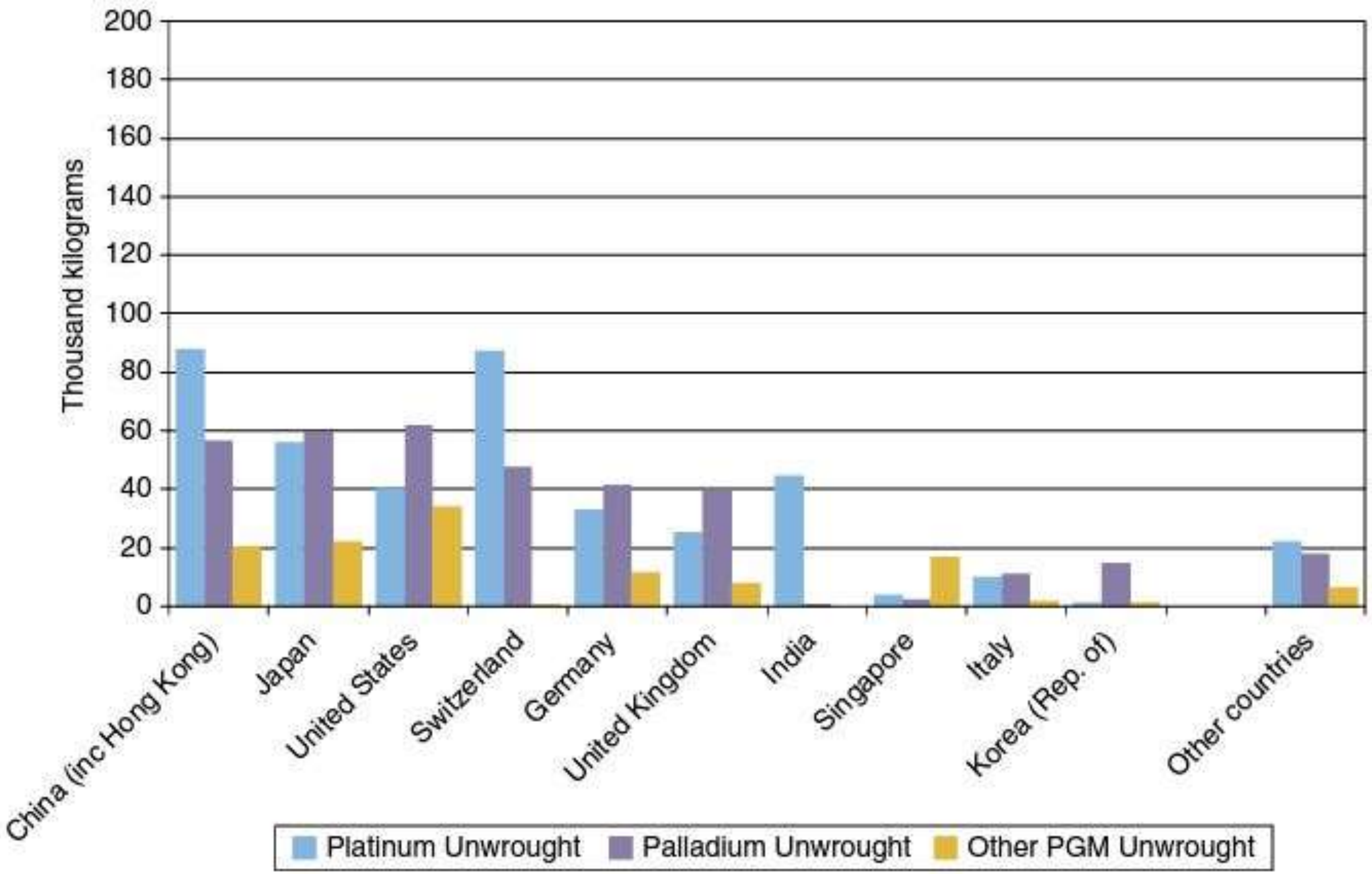


Figure 12.7 Major importers of platinum metal, concentrates and intermediate products, 2009. (Data from British Geological Survey World Mineral Statistics database and UN Comtrade, 2013.) (1 kilogram equals 32.151 troy ounces.)

PGM – prices

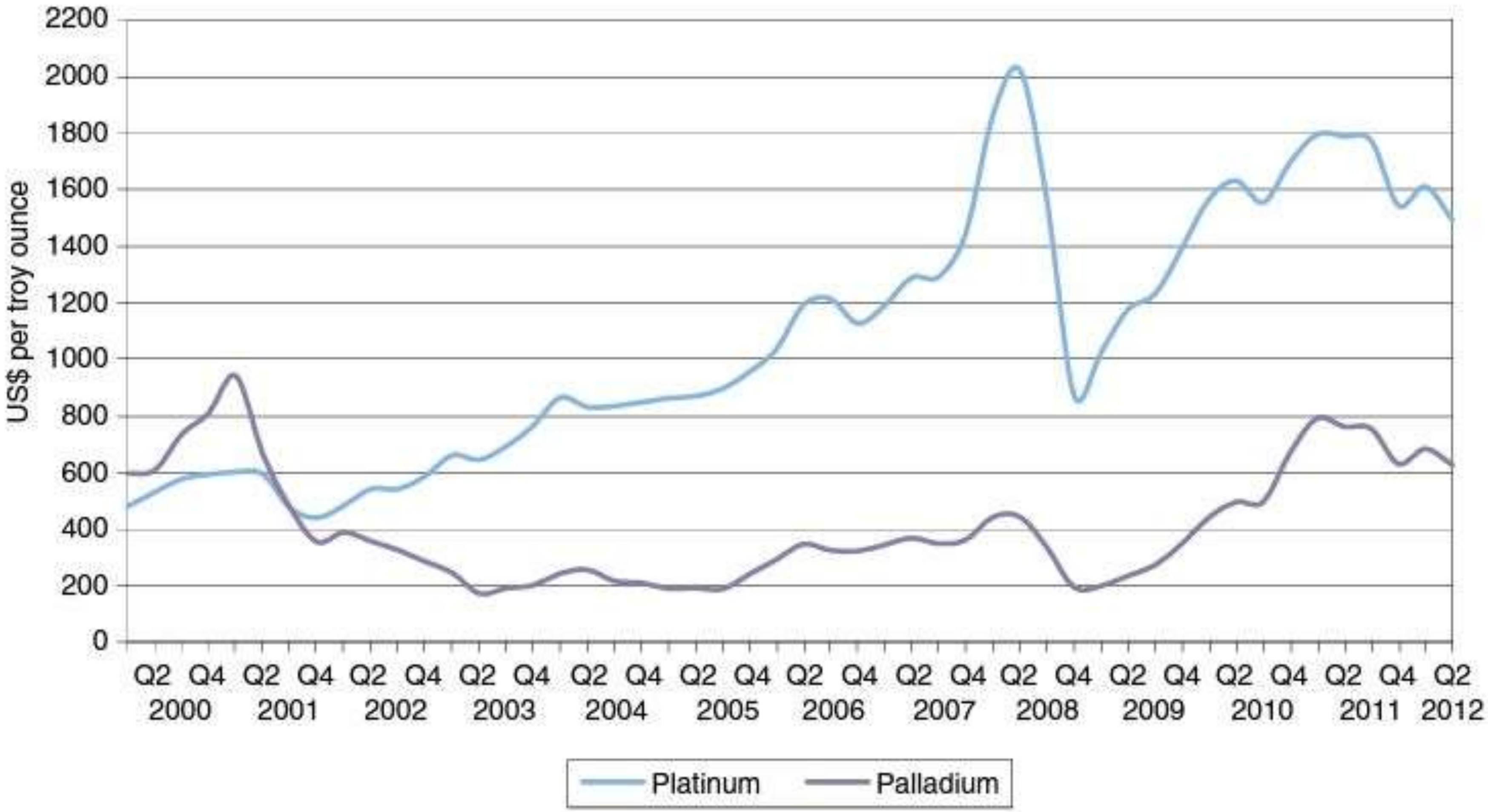
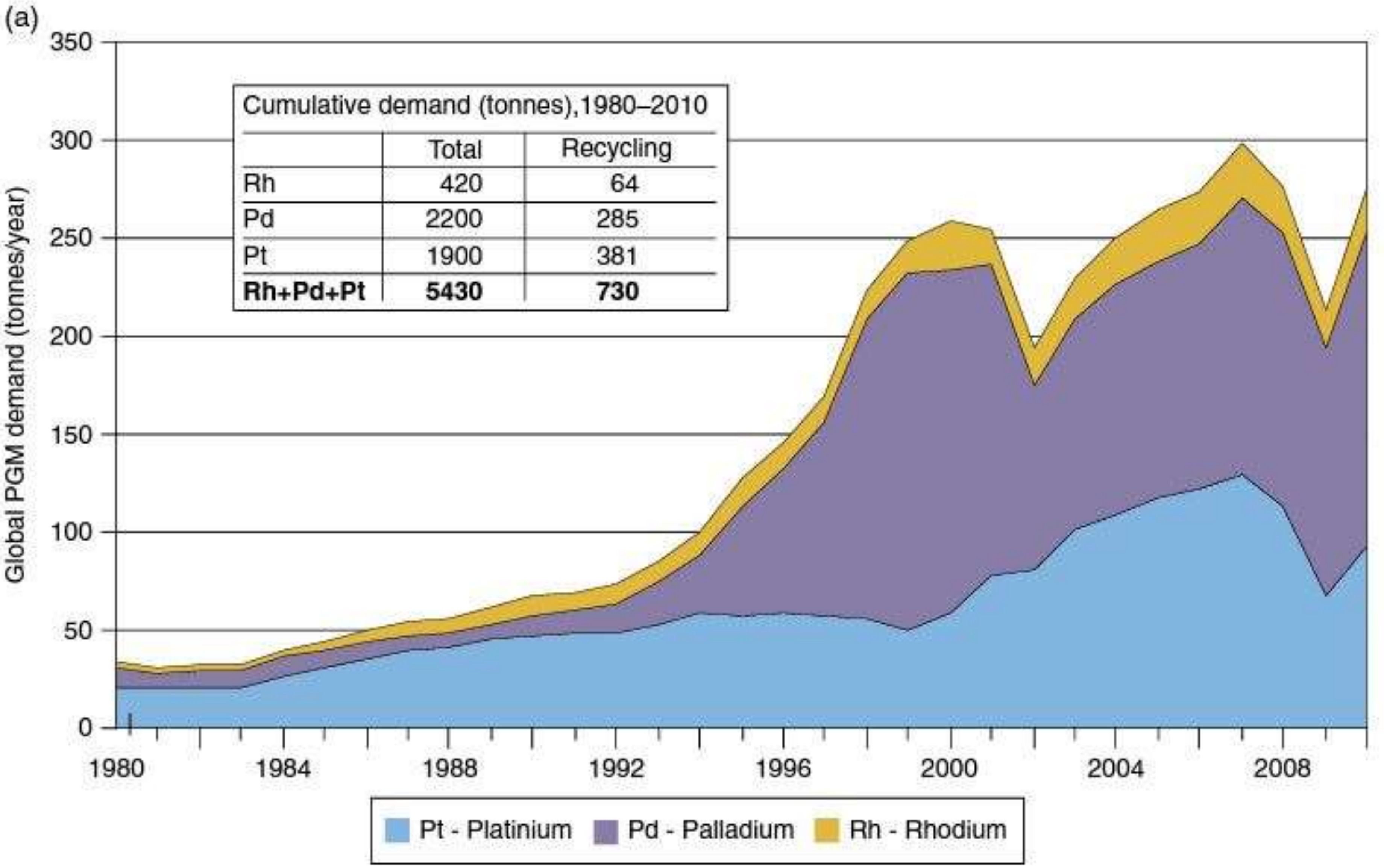


Figure 12.9 The prices of platinum and palladium between 2000 and end June 2012. (Johnson Matthey base price (unfabricated) US$ per troy ounce, quarterly average prices from Metal Bulletin.)

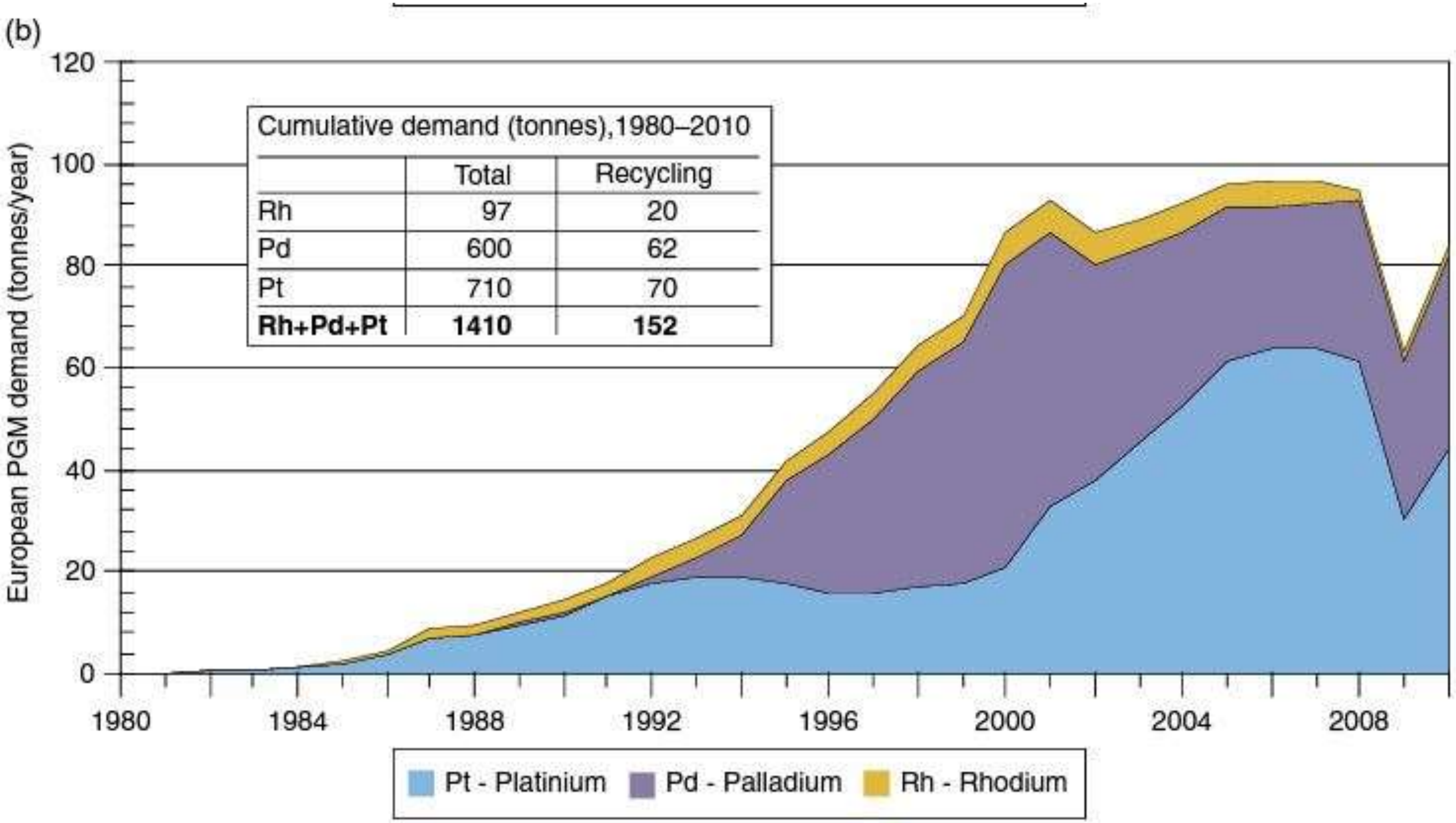
PGM – global PGM demand



Cumulative demand (tonnes),1980–2010

	Total	Recycling
Rh	420	64
Pd	2200	285
Pt	1900	381
Rh+Pd+Pt	**5430**	**730**

PGM – European PGM demand



Cumulative demand (tonnes),1980–2010

	Total	Recycling
Rh	97	20
Pd	600	62
Pt	710	70
Rh+Pd+Pt	**1410**	**152**

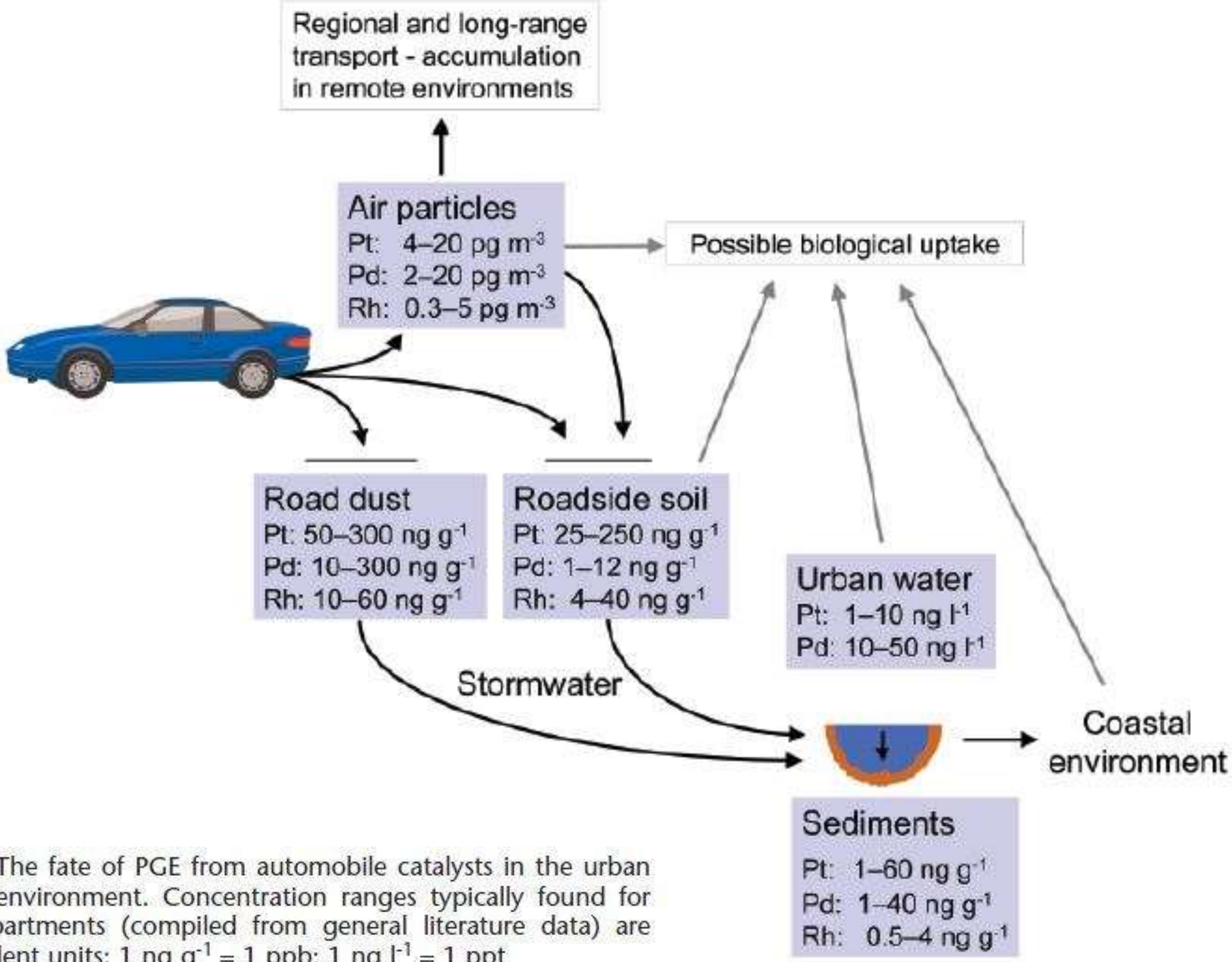
PGM – environmental issues

- In metallic form the PGM are generally regarded as **inert**, **non-toxic** and **non-allergenic**. However, some of their compounds, particularly certain PGM-chlorinated salts, are both **highly toxic** and **allergenic** (platinosis), and DNA damage due to PGM exposure has been reported.

- The greatly increased use of PGM in recent years has raised the level of PGM emissions into the environment (especially autocatalysts). **High PGM concentrations** have been recorded in dust, silt, soils and waters close to major **highways** and in **urban areas**. Furthermore, complexation of PGM derived from autocatalysts has been shown to give rise to **mobile species** with possible associated increase in **bioavailability**.

- The main environmental issues associated with the mining and processing of sulfide-bearing ores of any type, including PGM ores, include: the generation of **acid mine drainage**, **ore dumps**, treatment plant and **tailings release of associated trace elements** (As, Pb, Sb).

PGM – environmental issues



Regional and long-range transport - accumulation in remote environments

Air particles
Pt: 4–20 pg m^{-3}
Pd: 2–20 pg m^{-3}
Rh: 0.3–5 pg m^{-3}

Possible biological uptake

Road dust
Pt: 50–300 ng g^{-1}
Pd: 10–300 ng g^{-1}
Rh: 10–60 ng g^{-1}

Roadside soil
Pt: 25–250 ng g^{-1}
Pd: 1–12 ng g^{-1}
Rh: 4–40 ng g^{-1}

Urban water
Pt: 1–10 ng l^{-1}
Pd: 10–50 ng l^{-1}

Stormwater

Coastal environment

Sediments
Pt: 1–60 ng g^{-1}
Pd: 1–40 ng g^{-1}
Rh: 0.5–4 ng g^{-1}

The fate of PGE from automobile catalysts in the urban environment. Concentration ranges typically found for selected compartments (compiled from general literature data) are shown. Equivalent units: 1 ng g^{-1} = 1 ppb; 1 ng l^{-1} = 1 ppt

PGM – airborne particles in urban air

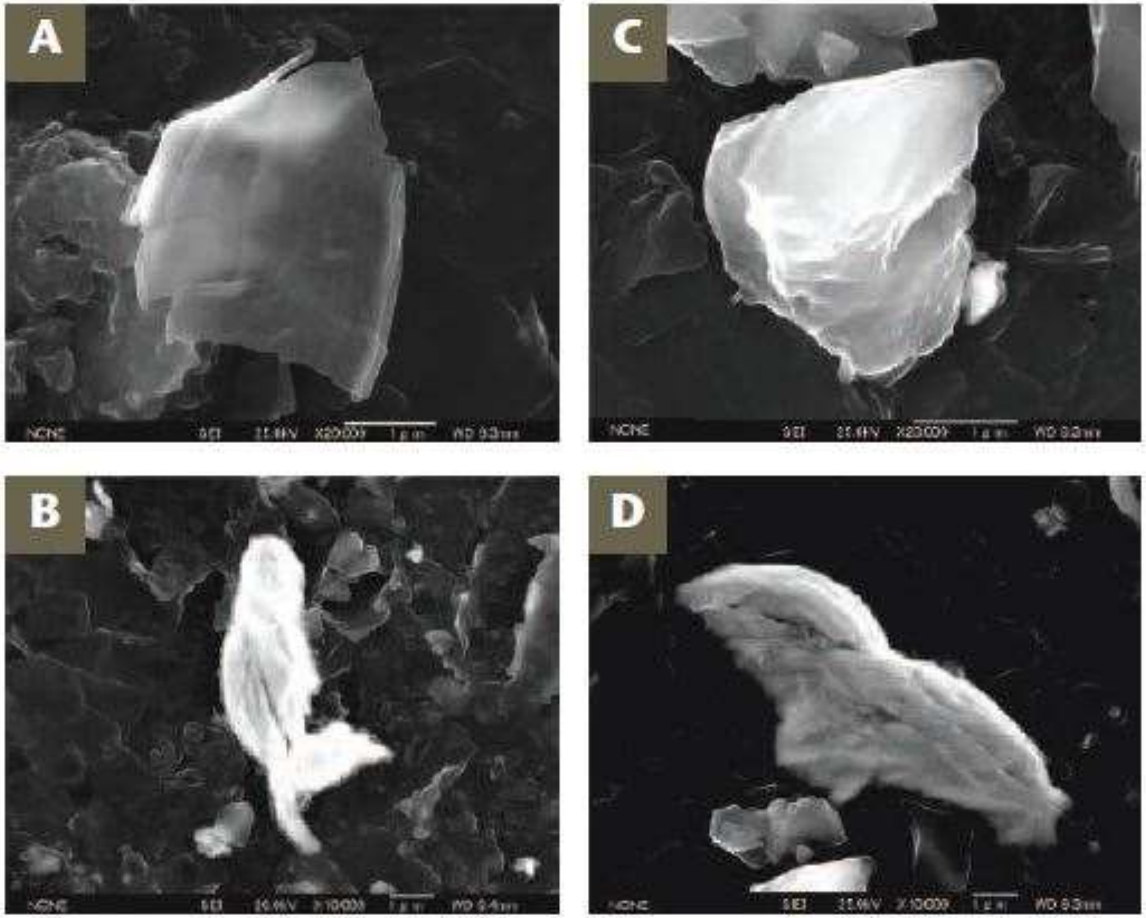


FIGURE 3 Field-emission scanning electron microscope images of PGE-containing particles in urban air in Göteborg, Sweden. Particles **A** and **C** contain only traces of Pt, with main components being Al, Si, and C. Particles **B** and **D** are enriched in Pt and Rh, and particle **B** is also rich in C. (IMAGES A, C AND D REPRODUCED WITH PERMISSION FROM *ENVIRONMENTAL SCIENCE & TECHNOLOGY* 2005, 39, 8156. COPYRIGHT AMERICAN CHEMICAL SOCIETY; PHOTOS COURTESY OF M. OWARI, UNIVERSITY OF TOKYO, JAPAN

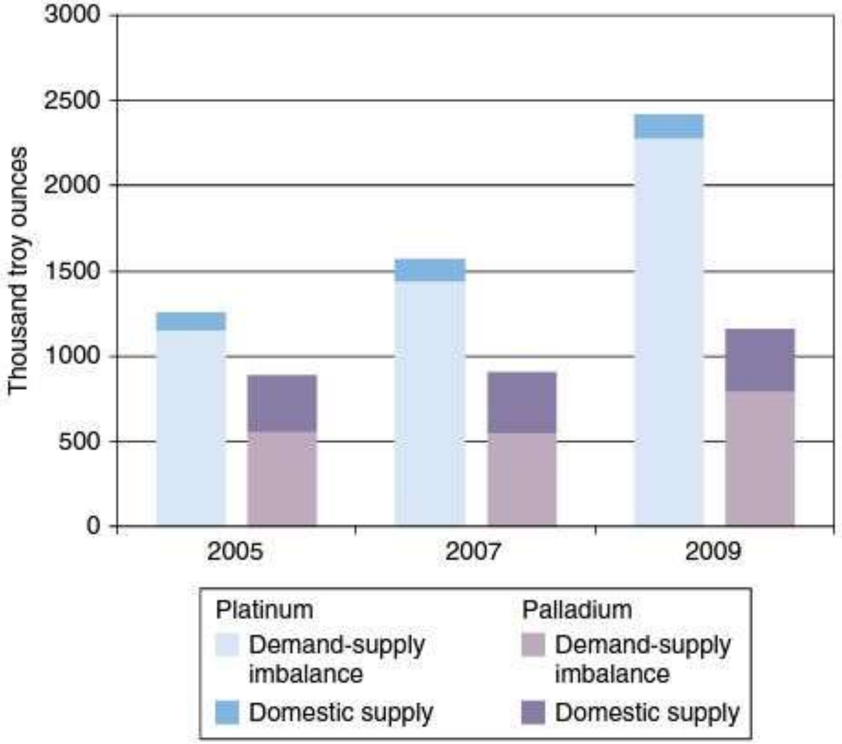
PGM – outlook

- **China** uses large and increasing quantities of PGM to support its rapidly growing economy, the modernisation of its industries and the spread of prosperity among its population (Pd for gasoline-powered vehicle fleet, jewellery, glass electronics, fuel cells, biomedical applications, superalloys, photovoltaics).

- The high level of concentration of PGM production in **South Africa** and **Russia** has given rise to concerns about supply security.

- **New supply** could be derived from mining PGM-dominant ores in Canada, Greenland, Australia and Brazil, although bringing new PGM production capacity on stream is a lengthy and expensive process.

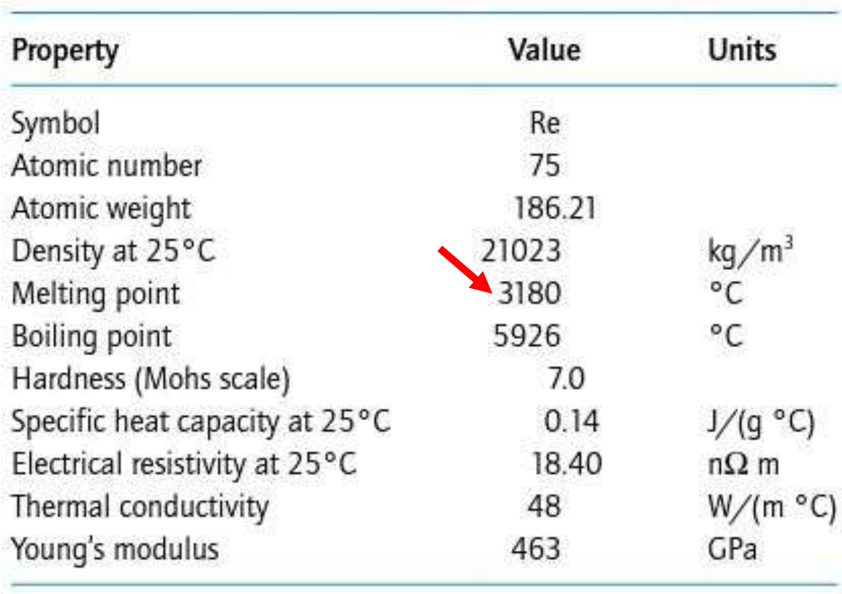
- Technical challenges related to mining and processing **new ore types** and **lower grade ores**, mining at **greater depths**, and **more efficient recycling**.



The consumption of platinum and palladium in China. (Data from CPM Group, 2011.)

Rhenium

Re – definitions and characteristics



Property	Value	Units
Symbol	Re	
Atomic number	75	
Atomic weight	186.21	
Density at 25°C	21023	kg/m^3
Melting point	3180	°C
Boiling point	5926	°C
Hardness (Mohs scale)	7.0	
Specific heat capacity at 25°C	0.14	J/(g °C)
Electrical resistivity at 25°C	18.40	nΩ m
Thermal conductivity	48	W/(m °C)
Young's modulus	463	GPa

- Re is reported by many sources to be the last element to be discovered. Its discovery in **1925** is credited to Ida Tacke, Walter Noddack and Otto Berg.

- Much of early work developing Re processing was done in the USA by Kennecott and many patents related to re recovery from **molybdenite** processing were granted to this company.

- Today the main use of Re is in **superalloys** for gas turbines in aircraft and in land-based applications, while its use in **petroleum-reforming catalysts** accounts for about 10% of total consumption.

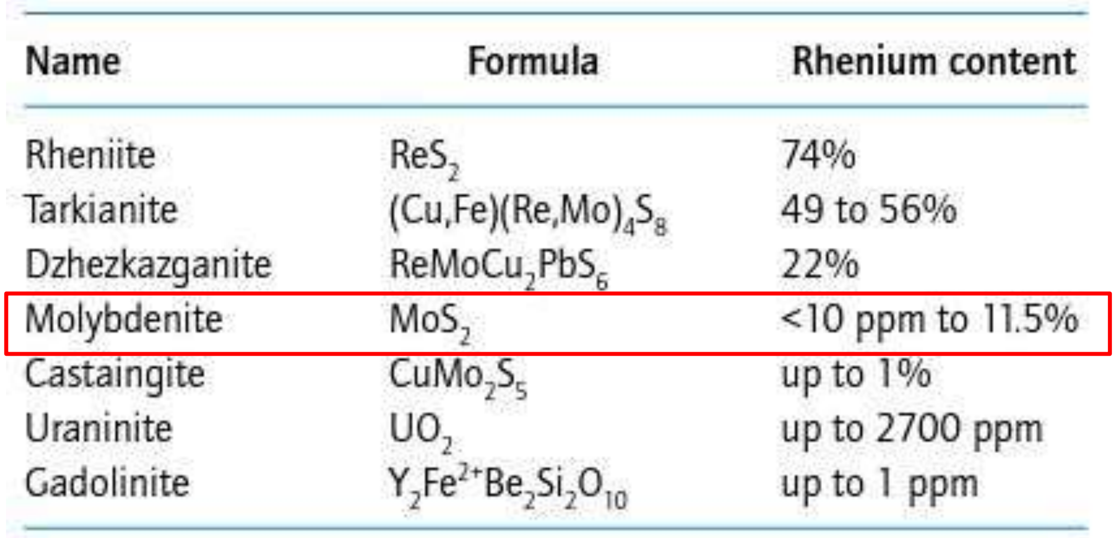
- Naturally occurring Re consists of two isotopes: **^{187}Re** (radioactive with a half-life of 4.3 x 10^{10} years) which accounts for 62.6% of the total, and **^{185}Re**, which makes up the balance of 37.4%.

- The chemical properties of Re resemble metals in the **Mn group** (Group 7) of the Periodic Table. The physical properties, however, are much more similar to those of the **refractory metals** of Groups 5 and 6, particularly **Mo** and **W**. Re is considered a **refractory metal** because of its **high melting point** (3180 °C). However, in contrast to other refractory metals, **Re does not form carbides**.

- Re exhibits **several valences** from -1 to + 7, with the most common being **+7**, **+6**, **+5** and **+ 4**. **It easily changes from one valence to another**, a property which makes it ideal for use as a **catalyst**.

Re – abundance in the Earth and mineralogy

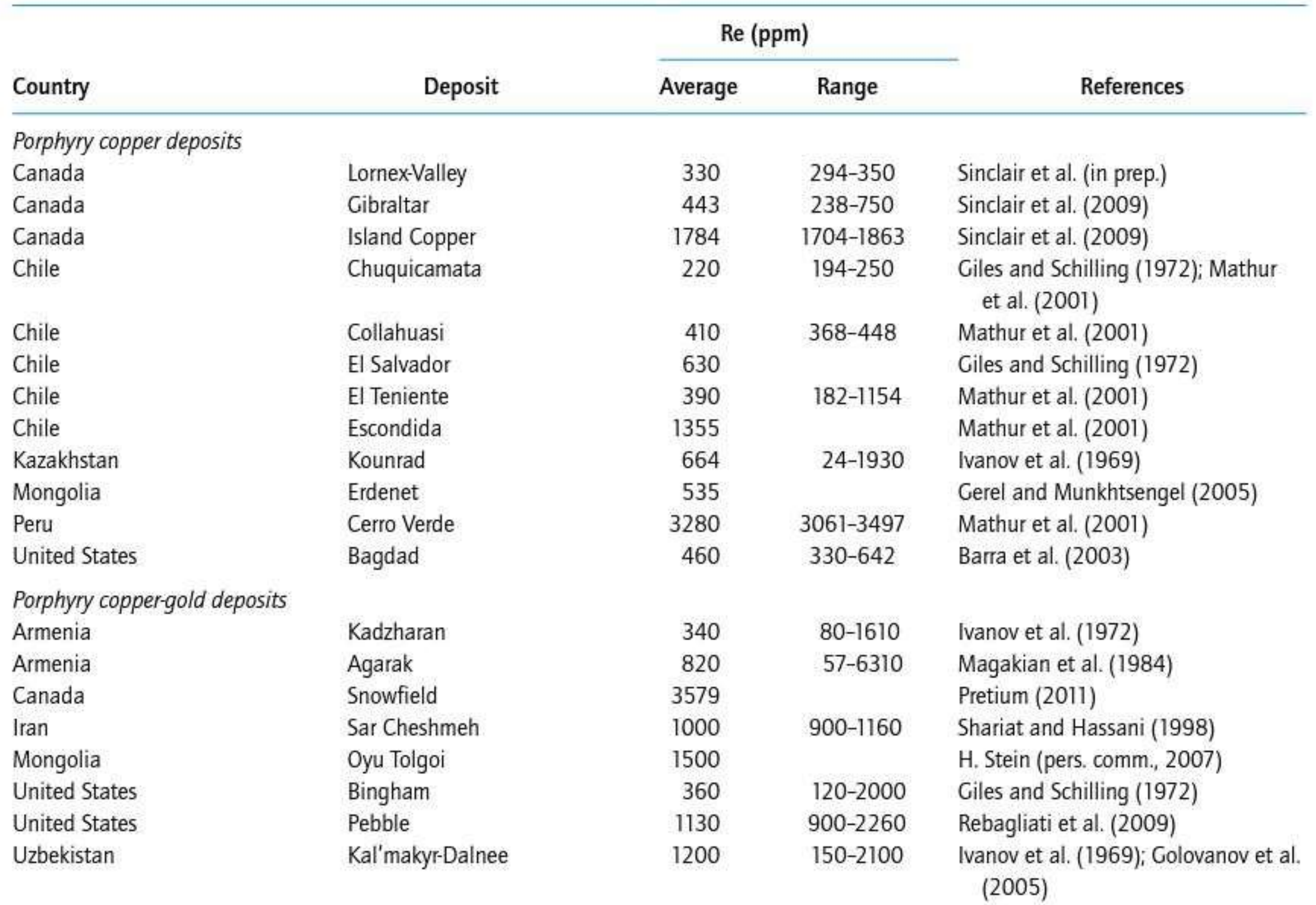
- **Re does not have a ductile-to-brittle transition temperature** → the addition of Re to W and Mo significantly reduces the brittle characteristics, increasing the **recrystallization T**, **ductility** and **ultimate tensile strength**.
- Re is one of the most dispersed elements, **Clarke 0.2 – 2 ppb**.
- Re minerals are also rare and relatively few minerals concentrate Re to a significant degree.



Name	Formula	Rhenium content
Rheniite	ReS_2	74%
Tarkianite	$(Cu,Fe)(Re,Mo)_4S_8$	49 to 56%
Dzhezkazganite	$ReMoCu_2PbS_6$	22%
Molybdenite	MoS_2	<10 ppm to 11.5%
Castaingite	$CuMo_2S_5$	up to 1%
Uraninite	UO_2	up to 2700 ppm
Gadolinite	$Y_2Fe^{2+}Be_2Si_2O_{10}$	up to 1 ppm

- Although Re has an **affinity for sulfide phases**, its concentration in most sulfide minerals is relatively low. However, the **ionic radius of Re^{4+} is very close to that of Mo^{4+}**, which allows for a limited substitution of Re for Mo in **molybdenite** and other Mo minerals, such as castaingite.
- **Re is similar geochemically to Mo**, which it commonly accompanies through magmatic and related hydrothermal processes, and is commonly concentrated in **molybdenite** with various types of granite-related deposits, particularly **porphyry deposits**. The Re content of most molybdenites is generally within a range of a **few ppm to several thousands of ppm** (typically 200 – 1000 ppm).
- Other minerals in which Re may be concentrated in significant levels (> 1ppm) include **uraninite** and **gadolinite**.

Re content of molybdenite in porphyry deposits



Country	Deposit	Re (ppm) Average	Re (ppm) Range	References
Porphyry copper deposits				
Canada	Lornex-Valley	330	294–350	Sinclair et al. (in prep.)
Canada	Gibraltar	443	238–750	Sinclair et al. (2009)
Canada	Island Copper	1784	1704–1863	Sinclair et al. (2009)
Chile	Chuquicamata	220	194–250	Giles and Schilling (1972); Mathur et al. (2001)
Chile	Collahuasi	410	368–448	Mathur et al. (2001)
Chile	El Salvador	630		Giles and Schilling (1972)
Chile	El Teniente	390	182–1154	Mathur et al. (2001)
Chile	Escondida	1355		Mathur et al. (2001)
Kazakhstan	Kounrad	664	24–1930	Ivanov et al. (1969)
Mongolia	Erdenet	535		Gerel and Munkhtsengel (2005)
Peru	Cerro Verde	3280	3061–3497	Mathur et al. (2001)
United States	Bagdad	460	330–642	Barra et al. (2003)
Porphyry copper-gold deposits				
Armenia	Kadzharan	340	80–1610	Ivanov et al. (1972)
Armenia	Agarak	820	57–6310	Magakian et al. (1984)
Canada	Snowfield	3579		Pretium (2011)
Iran	Sar Cheshmeh	1000	900–1160	Shariat and Hassani (1998)
Mongolia	Oyu Tolgoi	1500		H. Stein (pers. comm., 2007)
United States	Bingham	360	120–2000	Giles and Schilling (1972)
United States	Pebble	1130	900–2260	Rebagliati et al. (2009)
Uzbekistan	Kal'makyr-Dalnee	1200	150–2100	Ivanov et al. (1969); Golovanov et al. (2005)

Re content of molybdenite in porphyry and vein deposits

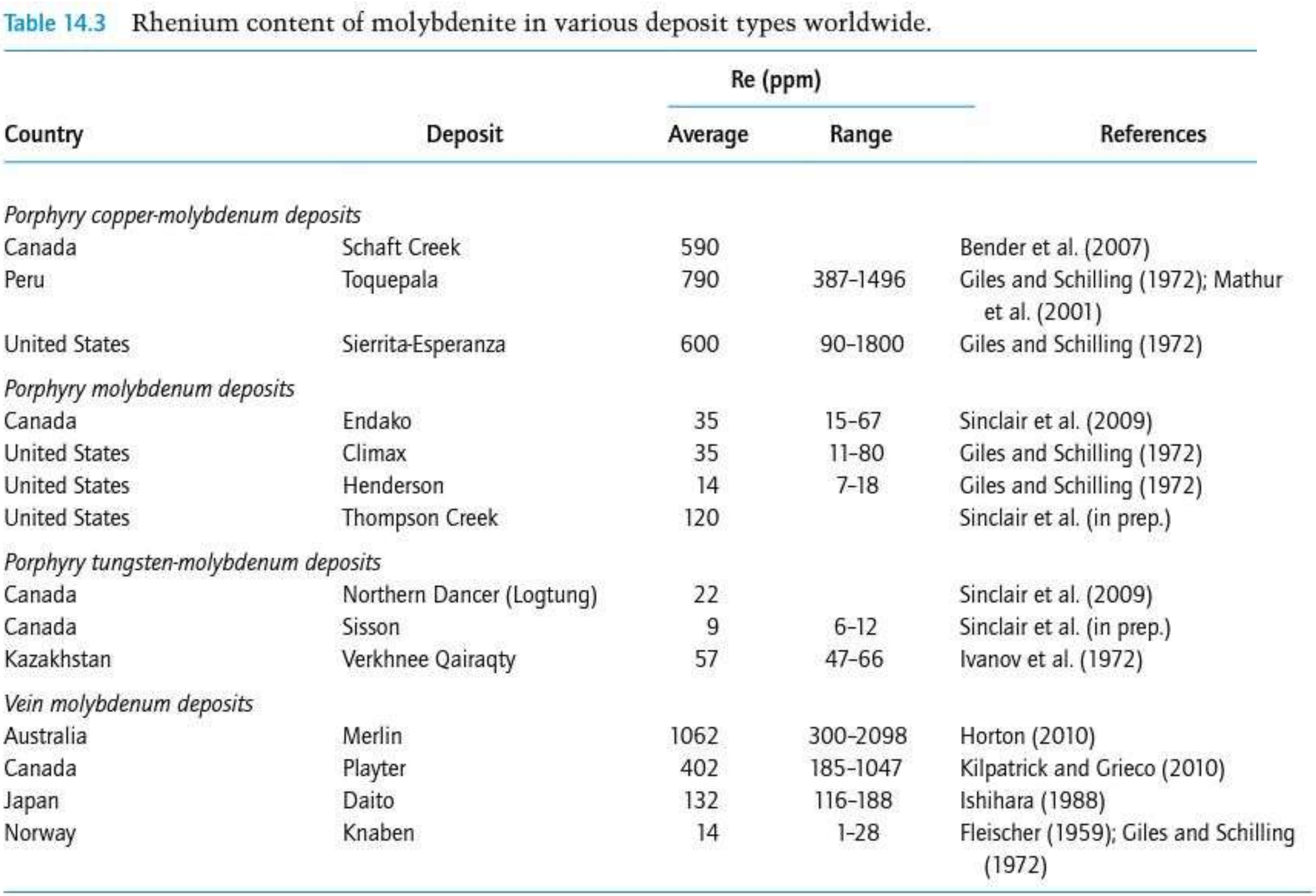


Table 14.3 Rhenium content of molybdenite in various deposit types worldwide.

Country	Deposit	Re (ppm) Average	Re (ppm) Range	References
Porphyry copper-molybdenum deposits				
Canada	Schaft Creek	590		Bender et al. (2007)
Peru	Toquepala	790	387–1496	Giles and Schilling (1972); Mathur et al. (2001)
United States	Sierrita-Esperanza	600	90–1800	Giles and Schilling (1972)
Porphyry molybdenum deposits				
Canada	Endako	35	15–67	Sinclair et al. (2009)
United States	Climax	35	11–80	Giles and Schilling (1972)
United States	Henderson	14	7–18	Giles and Schilling (1972)
United States	Thompson Creek	120		Sinclair et al. (in prep.)
Porphyry tungsten-molybdenum deposits				
Canada	Northern Dancer (Logtung)	22		Sinclair et al. (2009)
Canada	Sisson	9	6–12	Sinclair et al. (in prep.)
Kazakhstan	Verkhnee Qairaqty	57	47–66	Ivanov et al. (1972)
Vein molybdenum deposits				
Australia	Merlin	1062	300–2098	Horton (2010)
Canada	Playter	402	185–1047	Kilpatrick and Grieco (2010)
Japan	Daito	132	116–188	Ishihara (1988)
Norway	Knaben	14	1–28	Fleischer (1959); Giles and Schilling (1972)

Re – deposit types

- **Porphyry deposits** are **large**, **low-grade** deposits in which ore minerals occur in extensive zones of **fracturing** and **brecciation** associated with **porphyritic granitic intrusions**. They are the world's most important source of **Cu** and **Mo**, and are major sources of **Au** and **Ag**. They also account roughly **85-90% of primary Re production**. The average Re content of molybdenite from porphyry deposits varies from **< 10 ppm** to **4000 ppm**. **Porphyry Mo deposits** have the highest Mo grades (0.07 – 0.24% Mo) but the **lowest Re content** in molybdenites (10- 100 ppm).

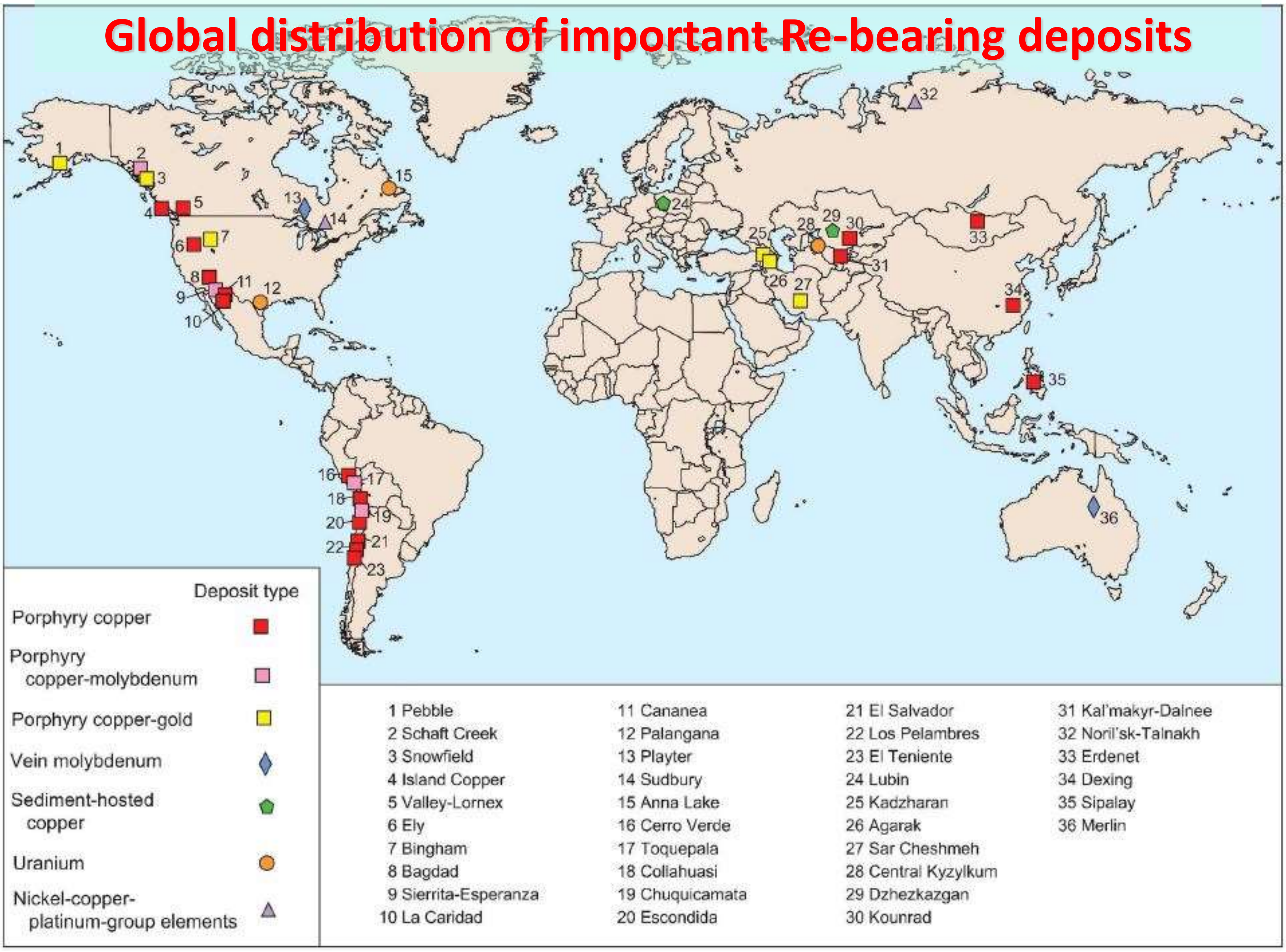
- **Vein deposits** occur in various structural settings such as **faults**, fault systems and **breccia zones** and, in some cases, include **replacement zones** in associated host rocks. Unlike porphyry deposits, they are typically **small**, but are **highly varied in size and metal contents**. In many vein deposits, molybdenite has Re content comparable to molybdenite from porphyry Mo deposits (< 100 ppm). The recently discovered **Merlin deposit (Australia)** contains an average of **1.3% Mo** and a **high Re content** in molybdenite.

- **Sediment-hosted Cu deposits** consist of **disseminated** to **veinlet** Cu sulfides that occur in zones **more or less concordant with the stratification** of their sedimentary host rocks. Re is recovered from the processing of Cu concentrates (chalcopyrite, bornite and chalcocite).

- **Uranium deposits**: the Re content varies from **< 1 to 5 ppm**. Re is closely **associated with Mo** (jordisite MoS_2, amorphous), but some Re may be also present in **U minerals** (uraninite UO_2).

- **Magmatic Ni-Cu-PGE deposits**: potentially significant source of Re (strong affinity for metallic or sulfide phases). E.g. Norilsk – Talnakh (Russia).

Global distribution of important Re-bearing deposits



Deposit type

- Porphyry copper 🟥
- Porphyry copper-molybdenum 🟪
- Porphyry copper-gold 🟨
- Vein molybdenum ◆
- Sediment-hosted copper ⬟
- Uranium 🟠
- Nickel-copper-platinum-group elements ▲

1 Pebble
2 Schaft Creek
3 Snowfield
4 Island Copper
5 Valley-Lornex
6 Ely
7 Bingham
8 Bagdad
9 Sierrita-Esperanza
10 La Caridad
11 Cananea
12 Palangana
13 Playter
14 Sudbury
15 Anna Lake
16 Cerro Verde
17 Toquepala
18 Collahuasi
19 Chuquicamata
20 Escondida
21 El Salvador
22 Los Pelambres
23 El Teniente
24 Lubin
25 Kadzharan
26 Agarak
27 Sar Cheshmeh
28 Central Kyzylkum
29 Dzhezkazgan
30 Kounrad
31 Kal'makyr-Dalnee
32 Noril'sk-Talnakh
33 Erdenet
34 Dexing
35 Sipalay
36 Merlin

Re content in molybdenite vs. Mo grade in porphyry deposits

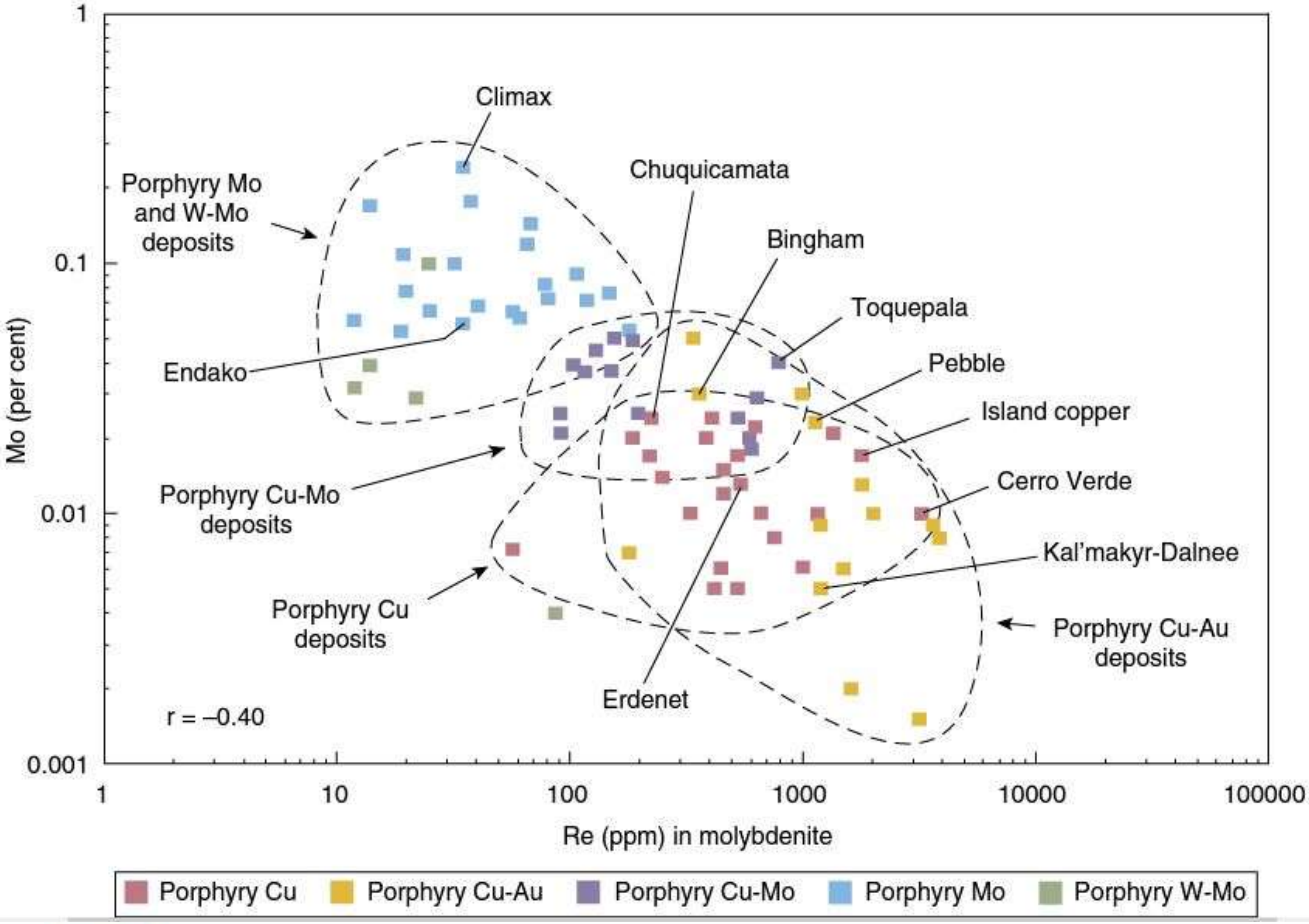


Figure 14.2 Rhenium content of molybdenite versus molybdenum grade in porphyry deposits. (Revised after Sinclair et al., 2009.) (Cu, copper; Mo, molybdenum; Au, gold; W, tungsten)

Re grade vs. tonnage

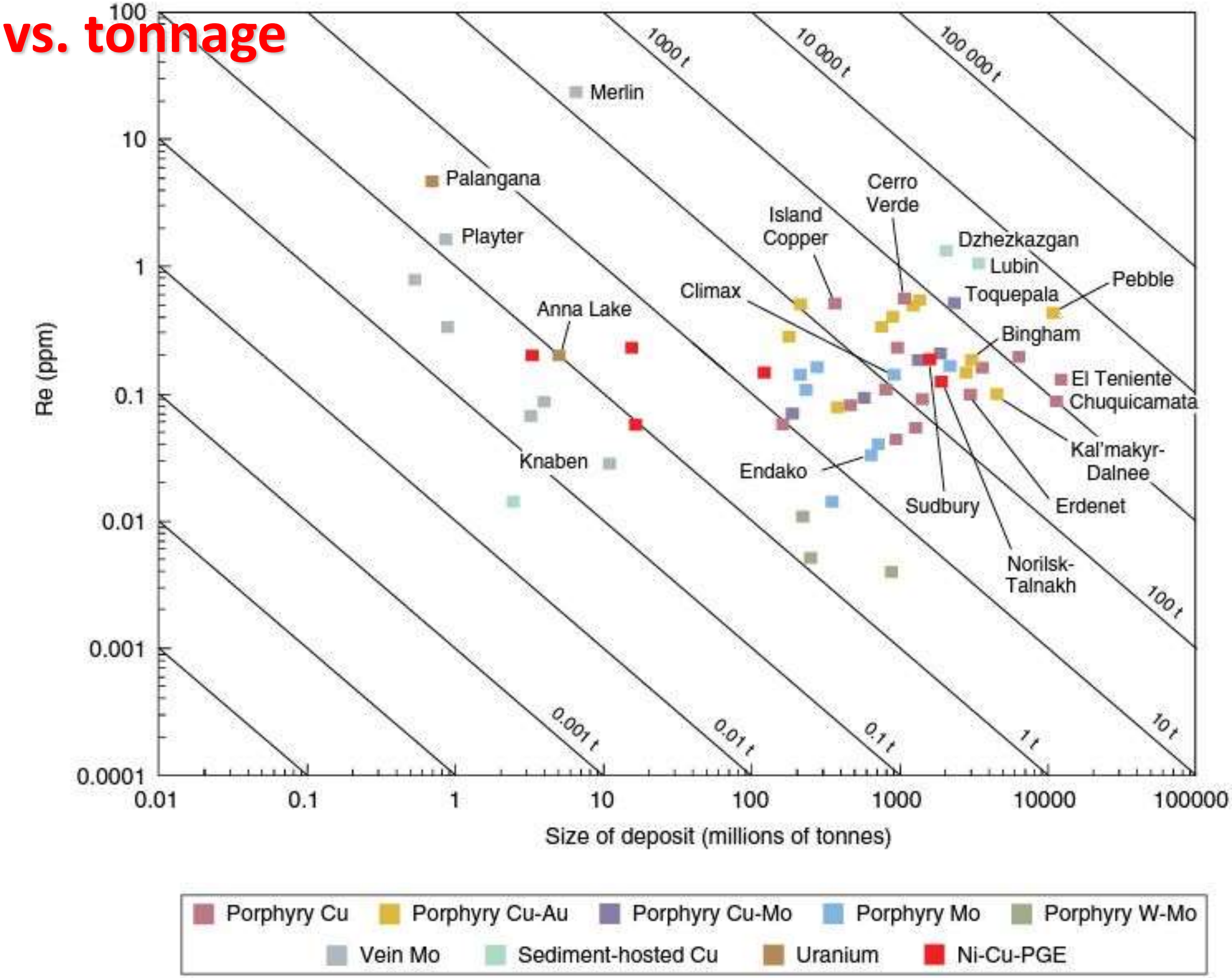
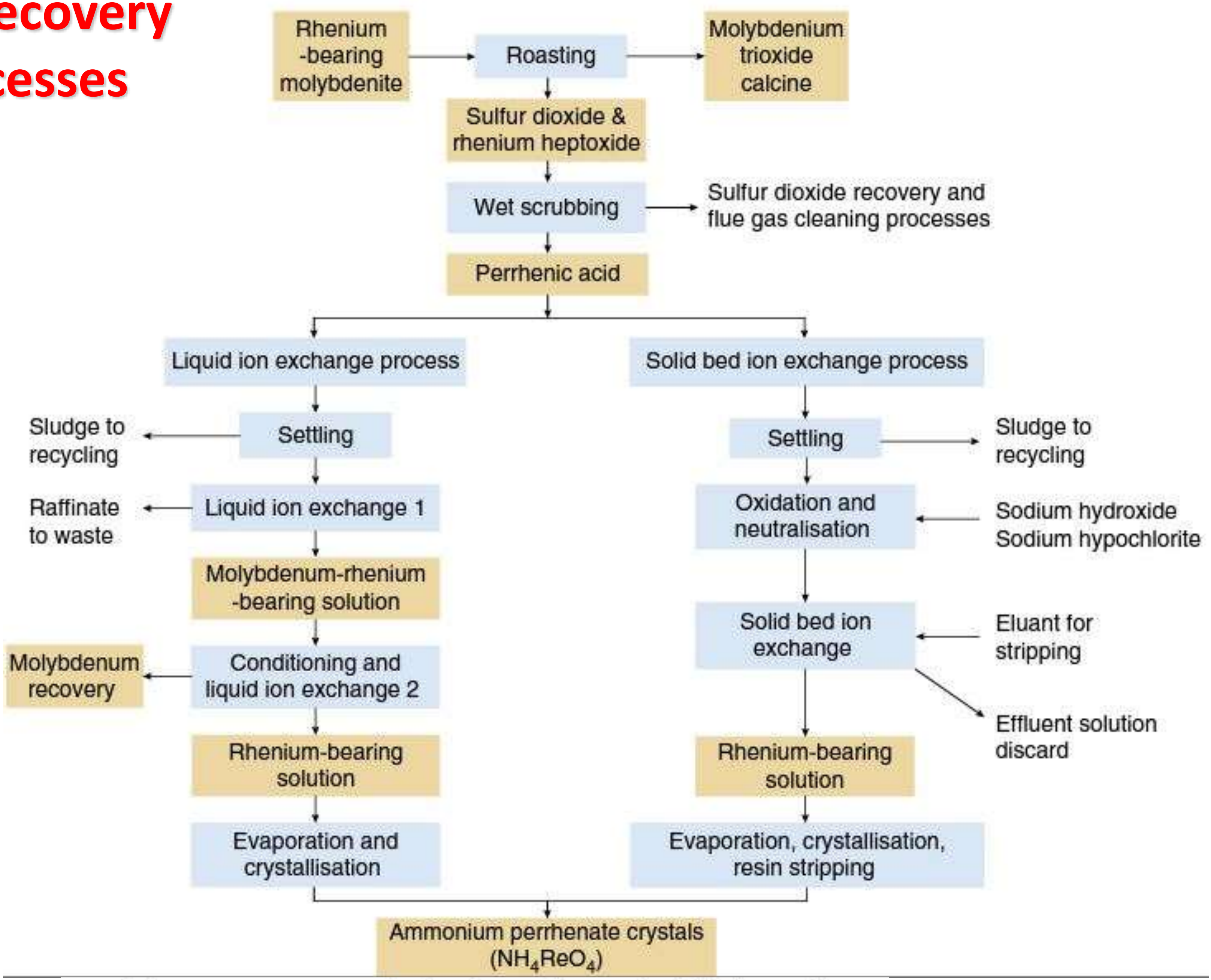


Figure 14.5 Rhenium grade versus tonnage of significant rhenium-bearing deposits; diagonal lines represent tonnes (t) of contained rhenium. (Revised after Sinclair et al., 2009.) (Cu, copper; Mo, molybdenum; Au, gold; W, tungsten; Ni, nickel; PGE, platinum-group elements)

Re – recovery processes



Rhenium -bearing molybdenite

Roasting

Molybdenium trioxide calcine

Sulfur dioxide & rhenium heptoxide

Wet scrubbing

Sulfur dioxide recovery and flue gas cleaning processes

Perrhenic acid

Liquid ion exchange process

Settling

Sludge to recycling

Liquid ion exchange 1

Raffinate to waste

Molybdenum-rhenium -bearing solution

Conditioning and liquid ion exchange 2

Molybdenum recovery

Rhenium-bearing solution

Evaporation and crystallisation

Solid bed ion exchange process

Settling

Sludge to recycling

Oxidation and neutralisation

Sodium hydroxide
Sodium hypochlorite

Solid bed ion exchange

Eluant for stripping

Effluent solution discard

Rhenium-bearing solution

Evaporation, crystallisation, resin stripping

Ammonium perrhenate crystals (NH_4ReO_4)

Typical rhenium recovery process by liquid ion exchange and solid-bed ion exchange.

Re – production

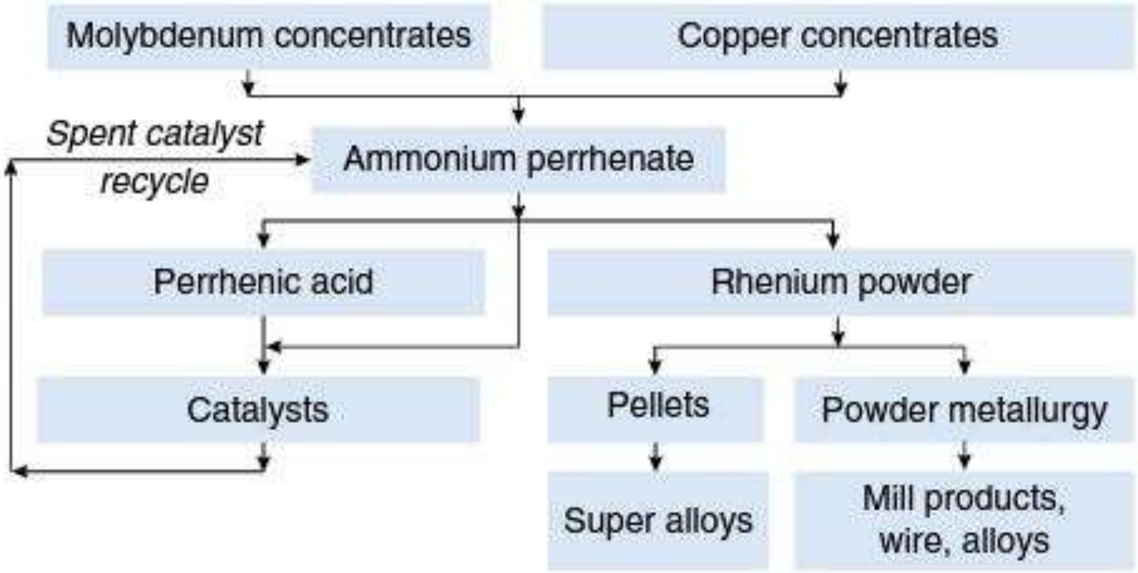


Figure 14.7 Summary of the production of rhenium and products.

- Re metal powder is produced by traditional powder metallurgy techniques. **Ammonium perrhenate** (**NH_4ReO_4**) is reduced using H in common boats-in-tubes type furnaces.

- Re for alloy production is produced by **pressing the powder into pellets** of varying size. The pellets then are **sintered** to improve physical integrity as well as to reduce gases further.

Re – specifications and uses

The main form of Re in which it is traded is **ammonium perrhenate** (APR, NH_4ReO_4), ready to be processed further for use in one of its 2 main industries:

1. **Superalloy** for casting into single-crystal turbine blades for aero-engines.
2. Solution for the manufacture of **reforming catalysts**.

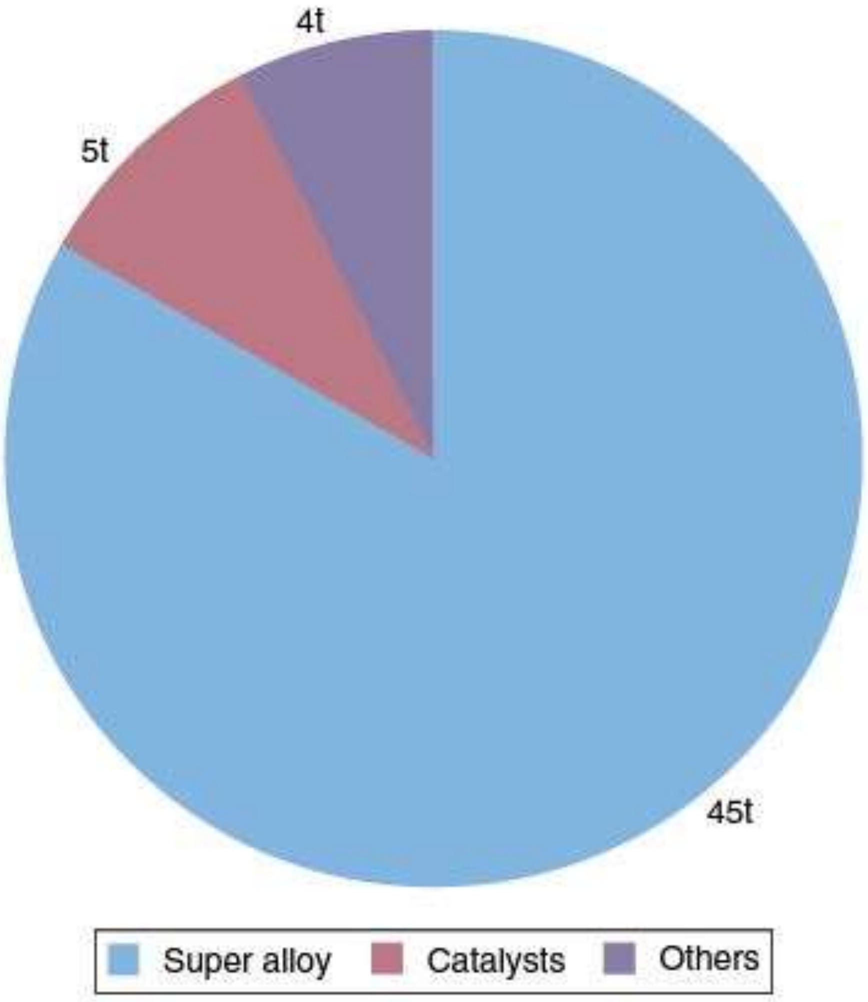


Figure 14.8 The main sectors of rhenium consumption in 2012 (tonnes). (Data from MMTA, 2012a, courtesy of Lipmann Walton & Co Ltd.)

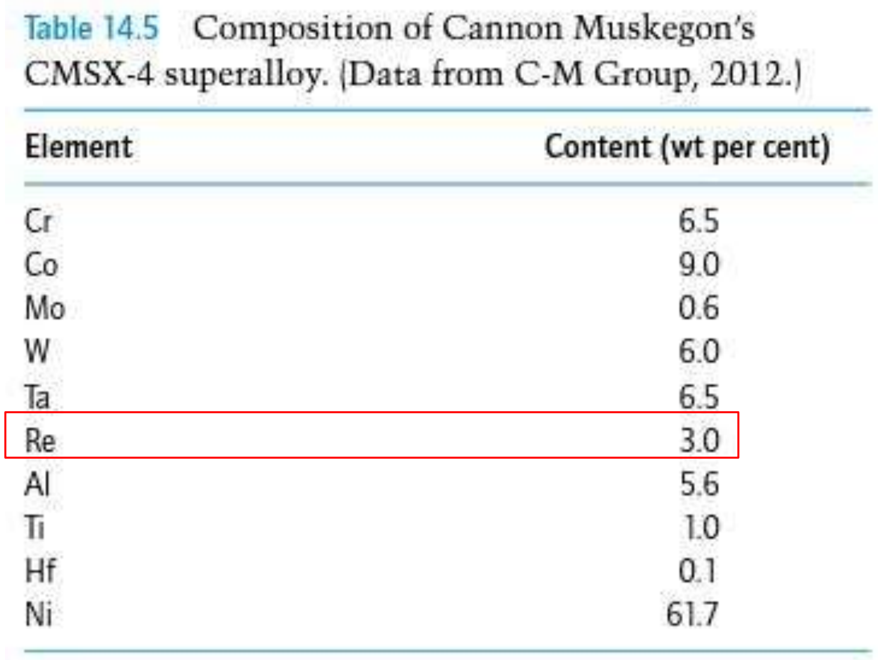


Table 14.5 Composition of Cannon Muskegon's CMSX-4 superalloy. (Data from C-M Group, 2012.)

Element	Content (wt per cent)
Cr	6.5
Co	9.0
Mo	0.6
W	6.0
Ta	6.5
Re	3.0
Al	5.6
Ti	1.0
Hf	0.1
Ni	61.7


Equiaxed Crystal Structure
Directionally Solidified Structure
Single Crystal
Increasing Resistance to Creep Deformation

Re – catalyst and superalloy grade

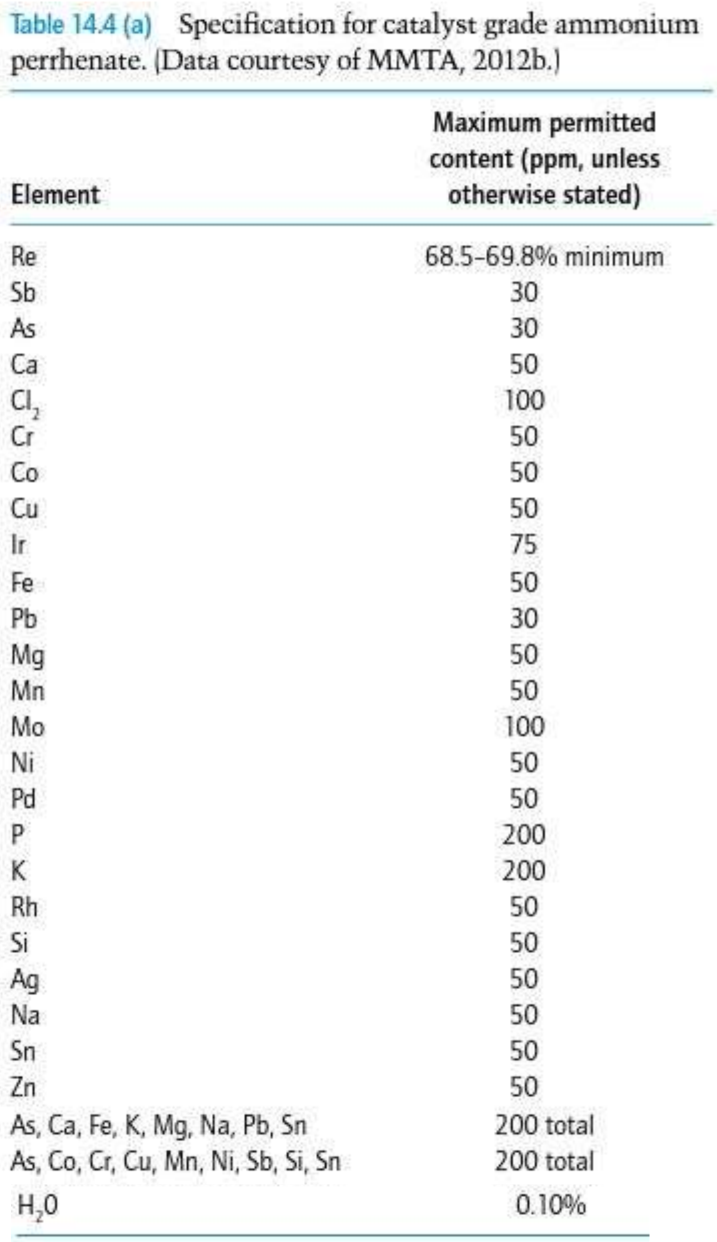


Table 14.4 (a) Specification for catalyst grade ammonium perrhenate. (Data courtesy of MMTA, 2012b.)

Element	Maximum permitted content (ppm, unless otherwise stated)
Re	68.5–69.8% minimum
Sb	30
As	30
Ca	50
Cl_2	100
Cr	50
Co	50
Cu	50
Ir	75
Fe	50
Pb	30
Mg	50
Mn	50
Mo	100
Ni	50
Pd	50
P	200
K	200
Rh	50
Si	50
Ag	50
Na	50
Sn	50
Zn	50
As, Ca, Fe, K, Mg, Na, Pb, Sn	200 total
As, Co, Cr, Cu, Mn, Ni, Sb, Si, Sn	200 total
H_2O	0.10%

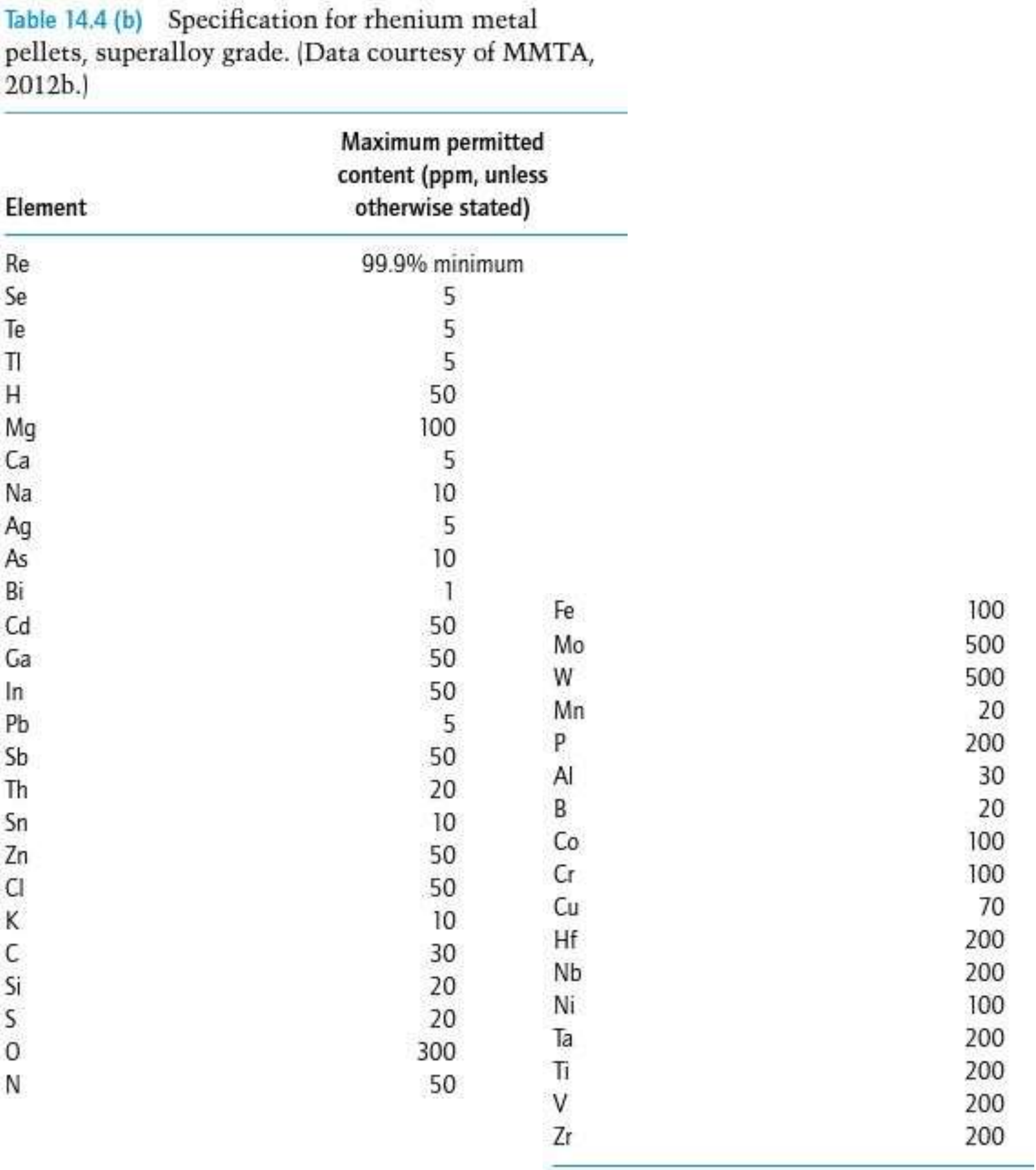


Table 14.4 (b) Specification for rhenium metal pellets, superalloy grade. (Data courtesy of MMTA, 2012b.)

Element	Maximum permitted content (ppm, unless otherwise stated)
Re	99.9% minimum
Se	5
Te	5
Tl	5
H	50
Mg	100
Ca	5
Na	10
Ag	5
As	10
Bi	1
Cd	50
Ga	50
In	50
Pb	5
Sb	50
Th	20
Sn	10
Zn	50
Cl	50
K	10
C	30
Si	20
S	20
O	300
N	50
Fe	100
Mo	500
W	500
Mn	20
P	200
Al	30
B	20
Co	100
Cr	100
Cu	70
Hf	200
Nb	200
Ni	100
Ta	200
Ti	200
V	200
Zr	200

Re – recycling and substitution

- **Recycling**
  - **Catalysts**: the value of Pt with which Re is allied (Pt 0.3% and Re 0.3%) provides the incentive for recycling (15 t Re per year).

  - **Superalloys**: the growth of a recycling industry has been slow and spasmodic (prices were mostly below the cost of recovery). The incentive for greater efficiency in recycling Re-bearing alloys came when Re reached USD 12000/kg. Two approaches are employed by recyclers:
    - **Chemical decomposition** of the complex alloy followed by an **ion-exchange** process to recover Re in the form of APR;
    - **Pyrophoric process** where Re is evaporated as the heptoxide and subsequently captured and then precipitated as APR.

- **Substitution**
  - **Re has non substitute** in its main use as a **3% constituent in complex Ni-based alloys** for **single-crystal turbine blades**. Here, the main purpose of Re is to increase the presence of the gamma prime (γ^{I}) phase which increases creep resistance.

  - In the **catalyst industry**, mono-metallic catalysts, consisting solely of Pt, are regularly used but, in most applications, Re is preferred alongside Pt because it increases efficiency.

Re – production

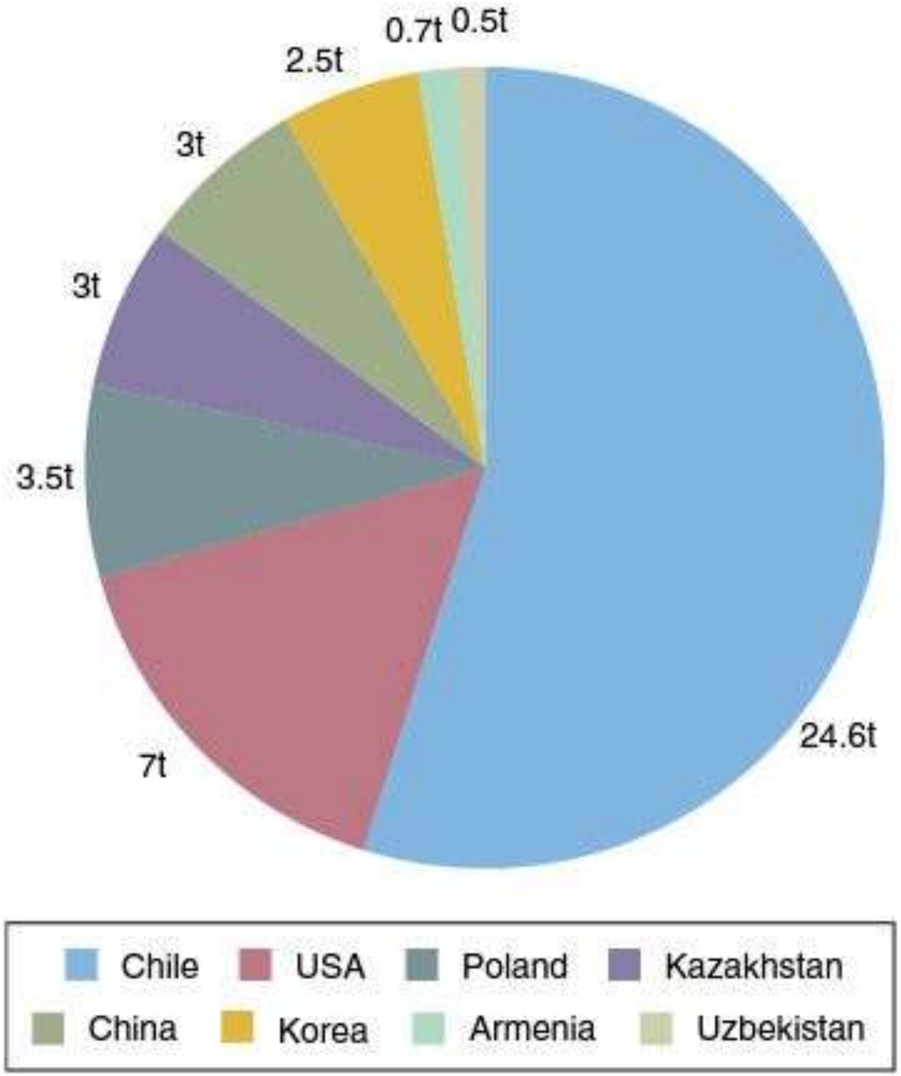


Figure 14.4 The main sources of primary rhenium production in 2012 (tonnes). (Data from MMTA, 2012a, courtesy of Lipmann Walton & Co Ltd.)

Re content in superalloys and prices

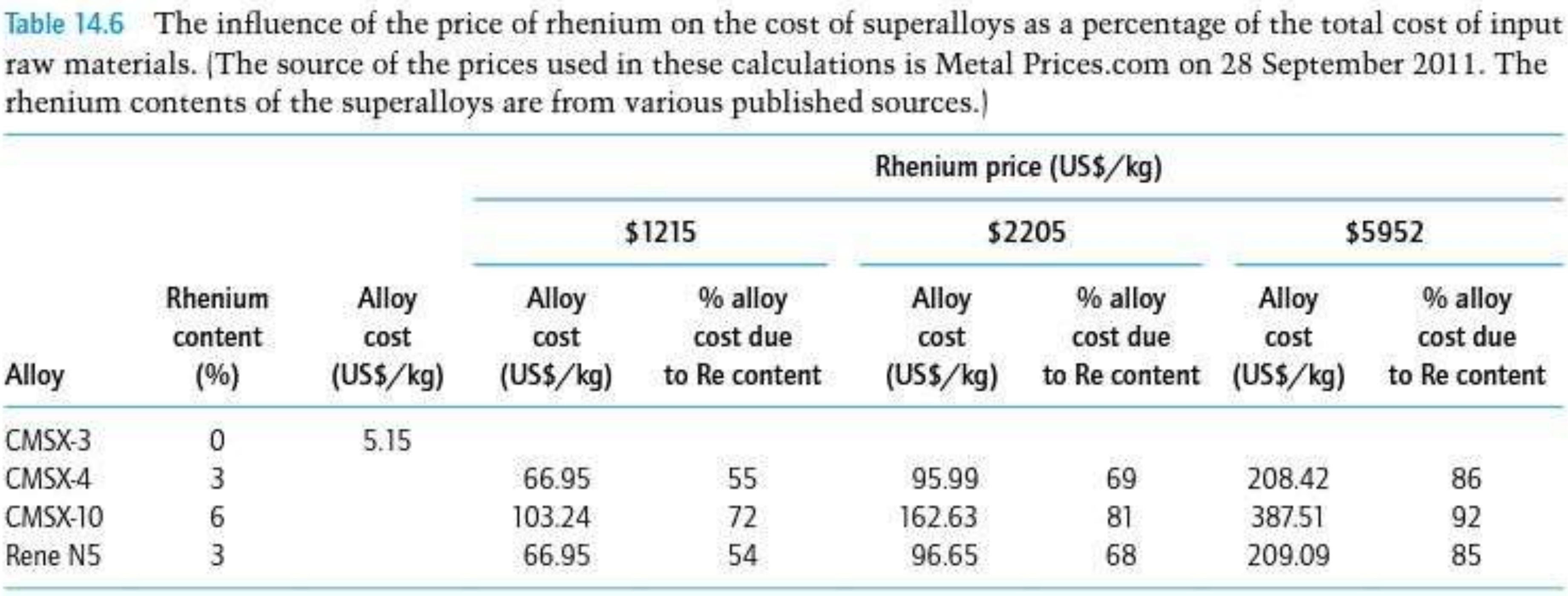
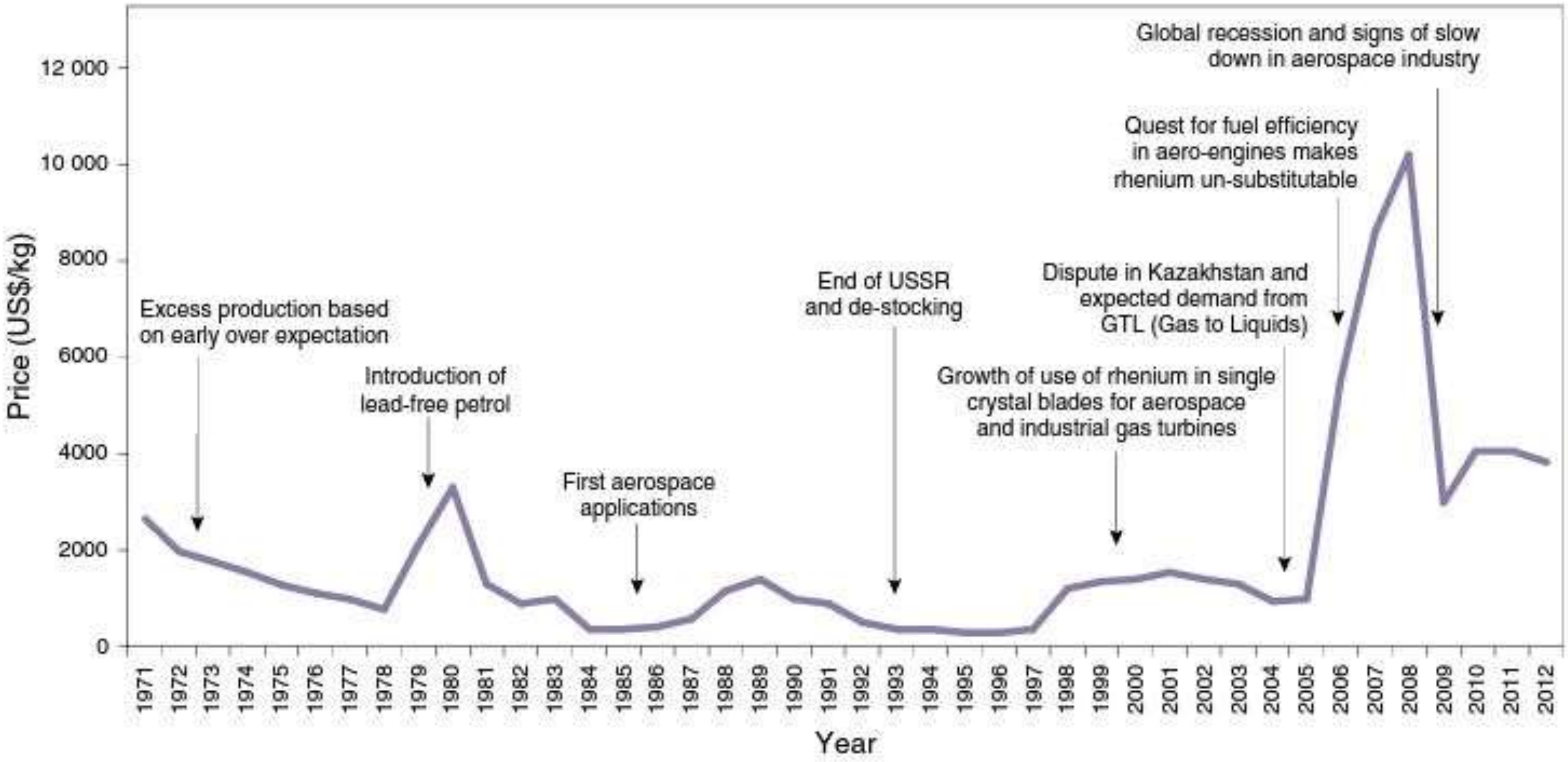


Table 14.6 The influence of the price of rhenium on the cost of superalloys as a percentage of the total cost of input raw materials. (The source of the prices used in these calculations is Metal Prices.com on 28 September 2011. The rhenium contents of the superalloys are from various published sources.)

			Rhenium price (US$/kg)					
			$1215		$2205		$5952	
Alloy	Rhenium content (%)	Alloy cost (US$/kg)	Alloy cost (US$/kg)	% alloy cost due to Re content	Alloy cost (US$/kg)	% alloy cost due to Re content	Alloy cost (US$/kg)	% alloy cost due to Re content
CMSX-3	0	5.15						
CMSX-4	3		66.95	55	95.99	69	208.42	86
CMSX-10	6		103.24	72	162.63	81	387.51	92
Rene N5	3		66.95	54	96.65	68	209.09	85

Re – price trend



Excess production based on early over expectation

Introduction of lead-free petrol

First aerospace applications

End of USSR and de-stocking

Growth of use of rhenium in single crystal blades for aerospace and industrial gas turbines

Dispute in Kazakhstan and expected demand from GTL (Gas to Liquids)

Quest for fuel efficiency in aero-engines makes rhenium un-substitutable

Global recession and signs of slow down in aerospace industry

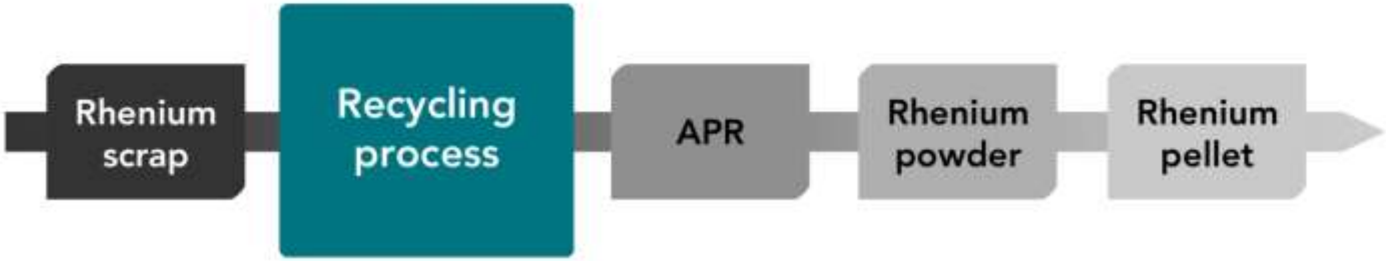
Figure 14.9 Rhenium price trend, 1971–2010. (Data from USGS up to 1993 and from Lipmann Walton & Co Ltd after 1993.)

Re – environmental issues

- Re is **radioactive** in all forms because of the content of the isotope **^{187}Re**. However, it decays by emission of very low energy β particles (electrons) that pose minimal risk to human health.

- Re contributes to high operating temperatures, increased fuel efficiency of gas turbines, reduction of nitrous oxide emissions, and blade longevity.

- The recovery of Re units from aerospace industry will never be as efficient as the catalyst industry due to the wide dispersal of re units in end-life blades, the cost of recovery and the length of time (up to 12 months) from the recycling of used blade to production of new Re pellet.



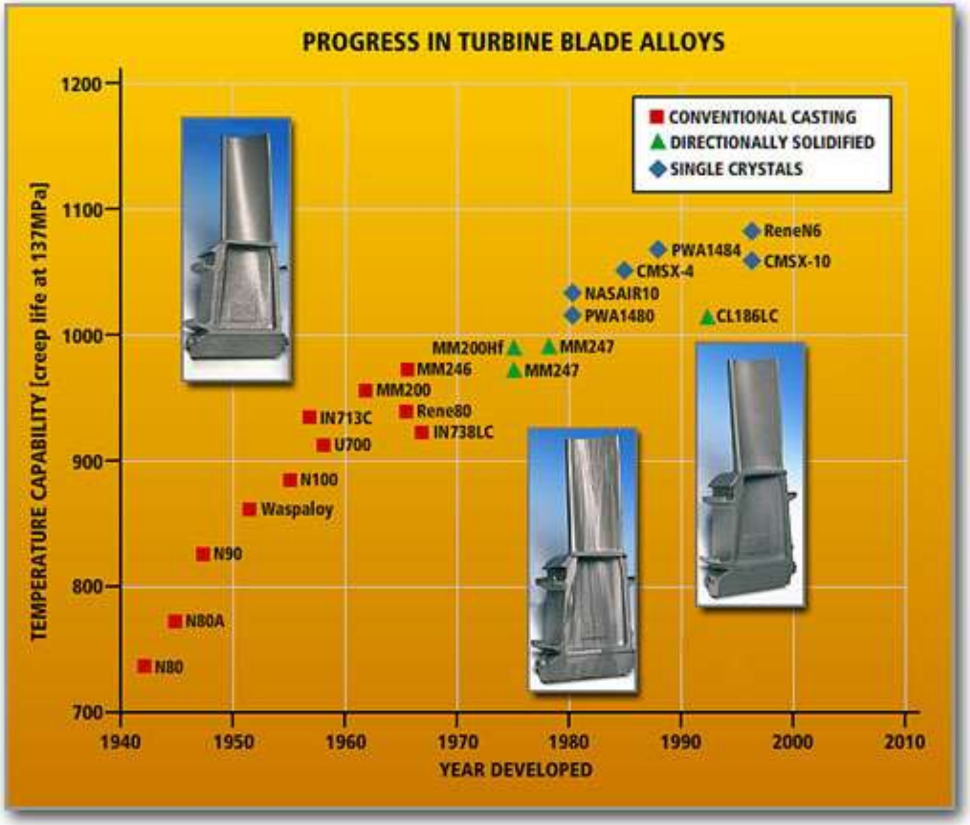
Re – outlook

- There seems to be **more Re coming available** now with offers from such as Uzbekistan for 500 kg per month of APR, recovery from Mongolian ores being toll roasted, as well as the promise of more from deposits yet to be mined such as Merlin in Australia and Pebble (Alaska).

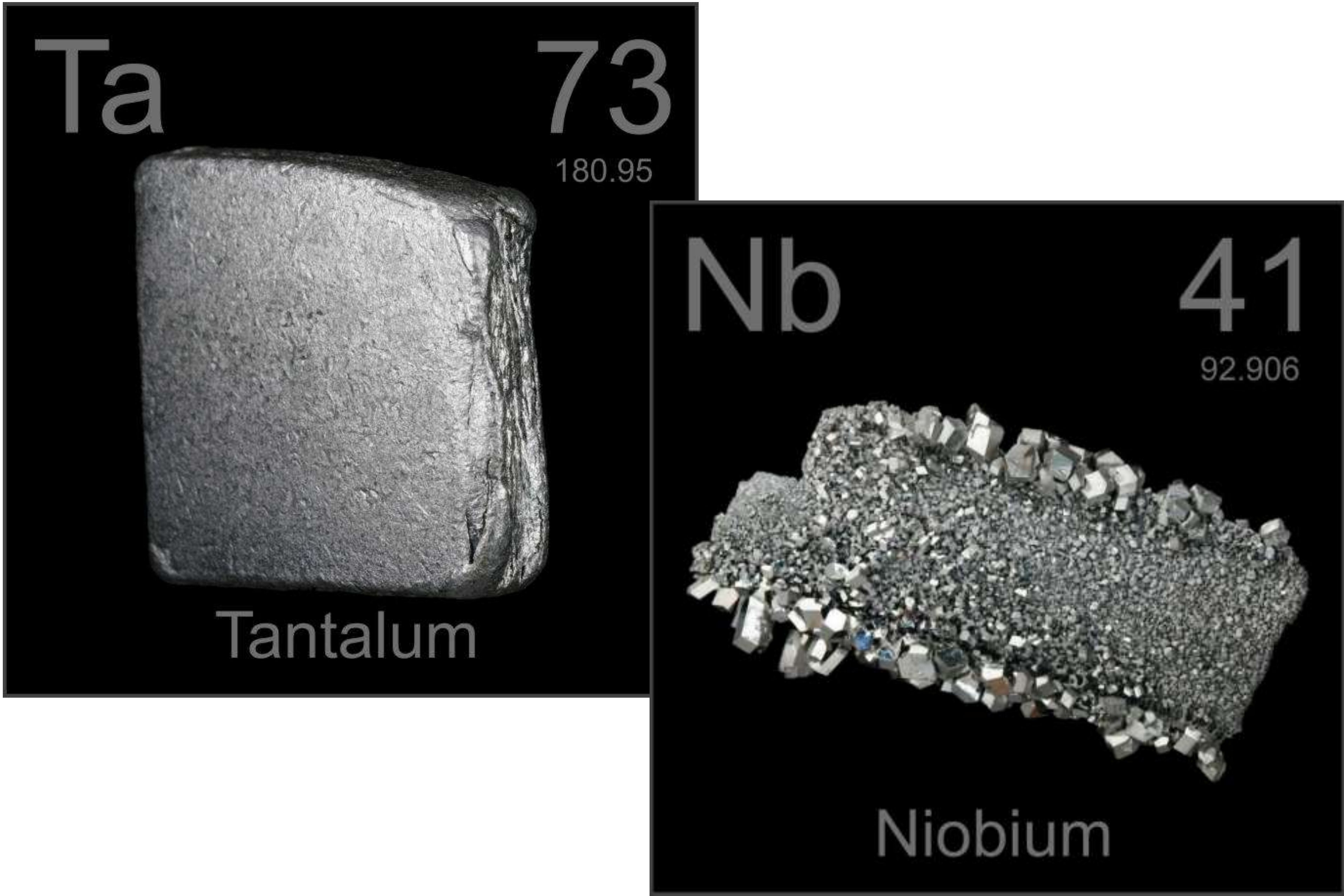
- The reduction of Re use by aircraft engine producers has resulted in increased Re availability for some of the other applications such as **land-based gas turbines** for use in **power generation**.

- The use of **X-ray tube target** production seems to be one area where Re demand is on the increase.

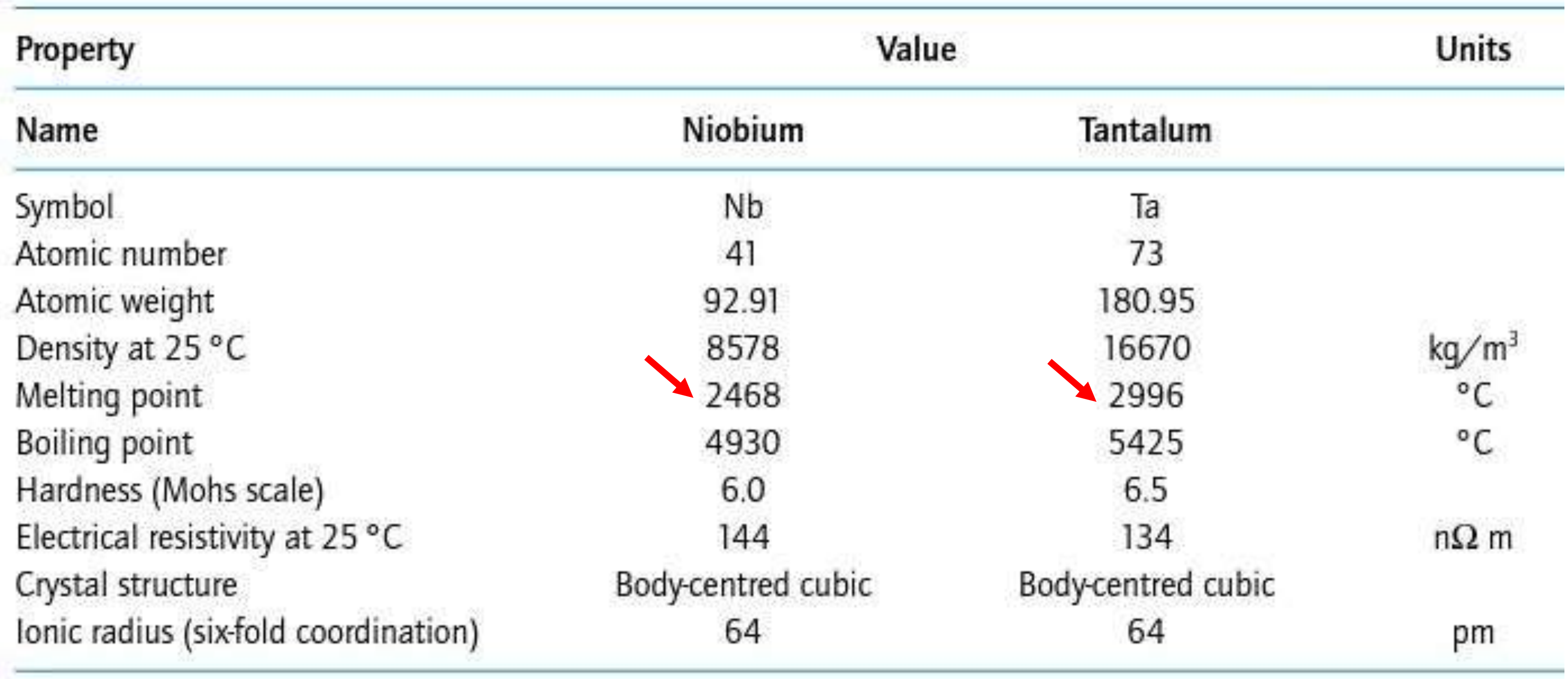
- Re used in Ni-based **superalloys** for the production of **single-crystal turbine blades** is set to remain rhenium's main market for many years to come.



Tantalum and niobium



Nb and Ta – definitions and characteristics



Property	Value		Units
Name	Niobium	Tantalum	
Symbol	Nb	Ta	
Atomic number	41	73	
Atomic weight	92.91	180.95	
Density at 25 °C	8578	16670	kg/m^3
Melting point	2468	2996	°C
Boiling point	4930	5425	°C
Hardness (Mohs scale)	6.0	6.5	
Electrical resistivity at 25 °C	144	134	nΩ m
Crystal structure	Body-centred cubic	Body-centred cubic	
Ionic radius (six-fold coordination)	64	64	pm

- Ta derives its name from king **Tantalus** in Greek mythology. His daughter was **Niobe**, after which the element Nb is named. In the geochemical literature, these elements are referred as “geochemical twins”, because their behavior is very similar.
- Charles Hatchett discovered Nb, first called columbium, in **1801**. Anders Gustav Ekeberg first discovered Ta in **1802**, but it was difficult to distinguish Ta from Nb. This issue was not resolved until Heinrich Rose in **1844** and Jean Charles Galissard de Marignac in 1866 were able to demonstrate that Nb and Ta were two different elements.

Nb and Ta – physical and chemical properties

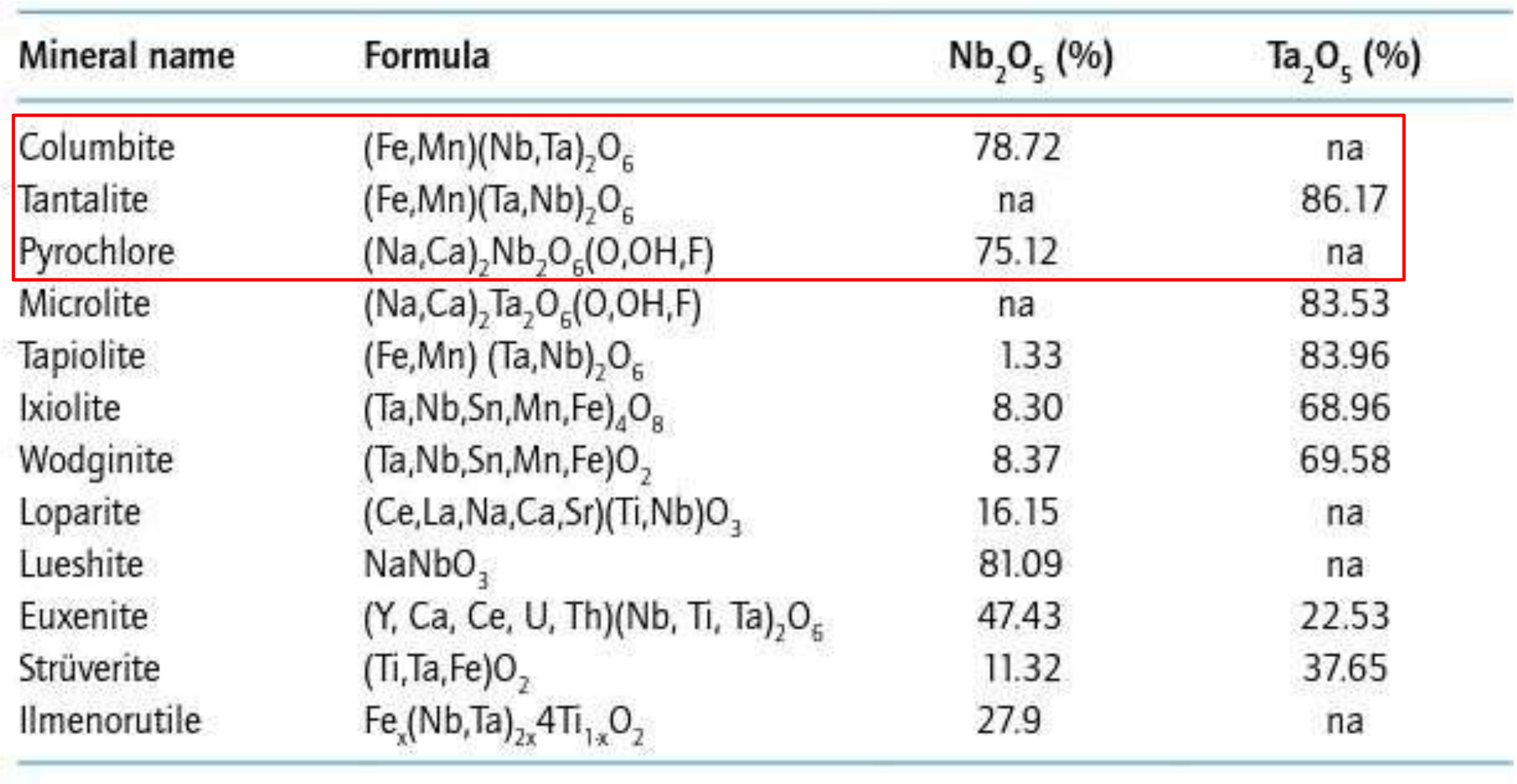
- Nb sits above Ta in the Periodic table and both have **very high melting temperatures**.
- **Nb has only one stable isotope ^{93}Nb**, but has **8 radiogenic isotopes** (^{89}Nb → ^{97}Nb).
- **Ta has two stable isotopes**: 99.988% occurs as **^{181}Ta** and 0.012% as **^{180}Ta**. It also has **6 radiogenic isotopes** (^{177}Ta → ^{183}Ta).
- Nb and Ta both have a **valency of +5** under most natural redox conditions and nearly the **same ionic radius**.
- These elements have a **high charge to ionic radius** and, because of this, they are **insoluble in most geological fluids**, are **strong Pearson acids** that are only complexed by strong ligands such as O^{2-}, OH^{-} and F^{-}. However, these elements are soluble at wt.% levels in **silicate melts**, particularly **alkaline melts**, and can attain even higher solubilities in **carbonatite melts**.

Nb and Ta – abundance in the Earth and mineralogy


Columbite - tantalite

- The estimated abundances of **Nb** and **Ta** in the upper continental crust are 12 and **0.9 ppm**, respectively, which is enriched relative to the bulk continental crust (Clarke), **8** and **0.7 ppm**, respectively. These values are much higher than the estimated concentrations in primitive mantle (548 ppb Nb and 40 ppb Ta).
- Both elements are **highly incompatible**, are **enriched in alkaline magmas** and are characteristically **depleted in calk-alkaline melts**.
- Apart from minerals of Nb, Ta and Sn, the highest concentrations of Nb and Ta are observed in **Ti-bearing minerals**, notably **rutile** TiO_2 and **titanite** $CaTiSiO_5$.
- Nb and Ta **do not occur naturally as free metals**. The **charge to ionic ratio** of Ta and Nb results in **strong bonds** being formed with **O**; in fact, most Nb-Ta minerals are oxides. The two most important groups of minerals by far are **columbotantalite** and **pyrochlore**.
- **Nb** deposits are predominantly hosted by **carbonatites** (→ **pyrochlore** group).
- **Ta** deposits are hosted by **peraluminous pegmatites** and **granites** [→ **columbotantalite**, **wodginite** $(Ta, Nb, Sn, Mn, Fe)_{16}O_{32}$ and **microlite** $(Na, Ca)_2(Ta, Nb)_2O_6(O, OH, F)$].

Nb and Ta – abundance in the Earth and mineralogy



Mineral name	Formula	Nb_2O_5 (%)	Ta_2O_5 (%)
Columbite	$(Fe,Mn)(Nb,Ta)_2O_6$	78.72	na
Tantalite	$(Fe,Mn)(Ta,Nb)_2O_6$	na	86.17
Pyrochlore	$(Na,Ca)_2Nb_2O_6(O,OH,F)$	75.12	na
Microlite	$(Na,Ca)_2Ta_2O_6(O,OH,F)$	na	83.53
Tapiolite	$(Fe,Mn)\ (Ta,Nb)_2O_6$	1.33	83.96
Ixiolite	$(Ta,Nb,Sn,Mn,Fe)_4O_8$	8.30	68.96
Wodginite	$(Ta,Nb,Sn,Mn,Fe)O_2$	8.37	69.58
Loparite	$(Ce,La,Na,Ca,Sr)(Ti,Nb)O_3$	16.15	na
Lueshite	$NaNbO_3$	81.09	na
Euxenite	$(Y, Ca, Ce, U, Th)(Nb, Ti, Ta)_2O_6$	47.43	22.53
Strüverite	$(Ti,Ta,Fe)O_2$	11.32	37.65
Ilmenorutile	$Fe_x(Nb,Ta)_{2x}4Ti_{1-x}O_2$	27.9	na

- The **columbotantalite group** minerals are the most common and contain both Nb and Ta ("**coltan**").
- Another source of Ta is as a **by-product of Sn mining** (cassiterite can contain wt.% of Ta and Nb).

Nb and Ta – deposit types

- All primary Nb and ta deposits are associated with **igneous rocks** and can be classified on the basis of the associated igneous rocks. Three types of deposits are recognised:

  1. **Carbonatite-hosted deposits** (**Nb** and industrial minerals).

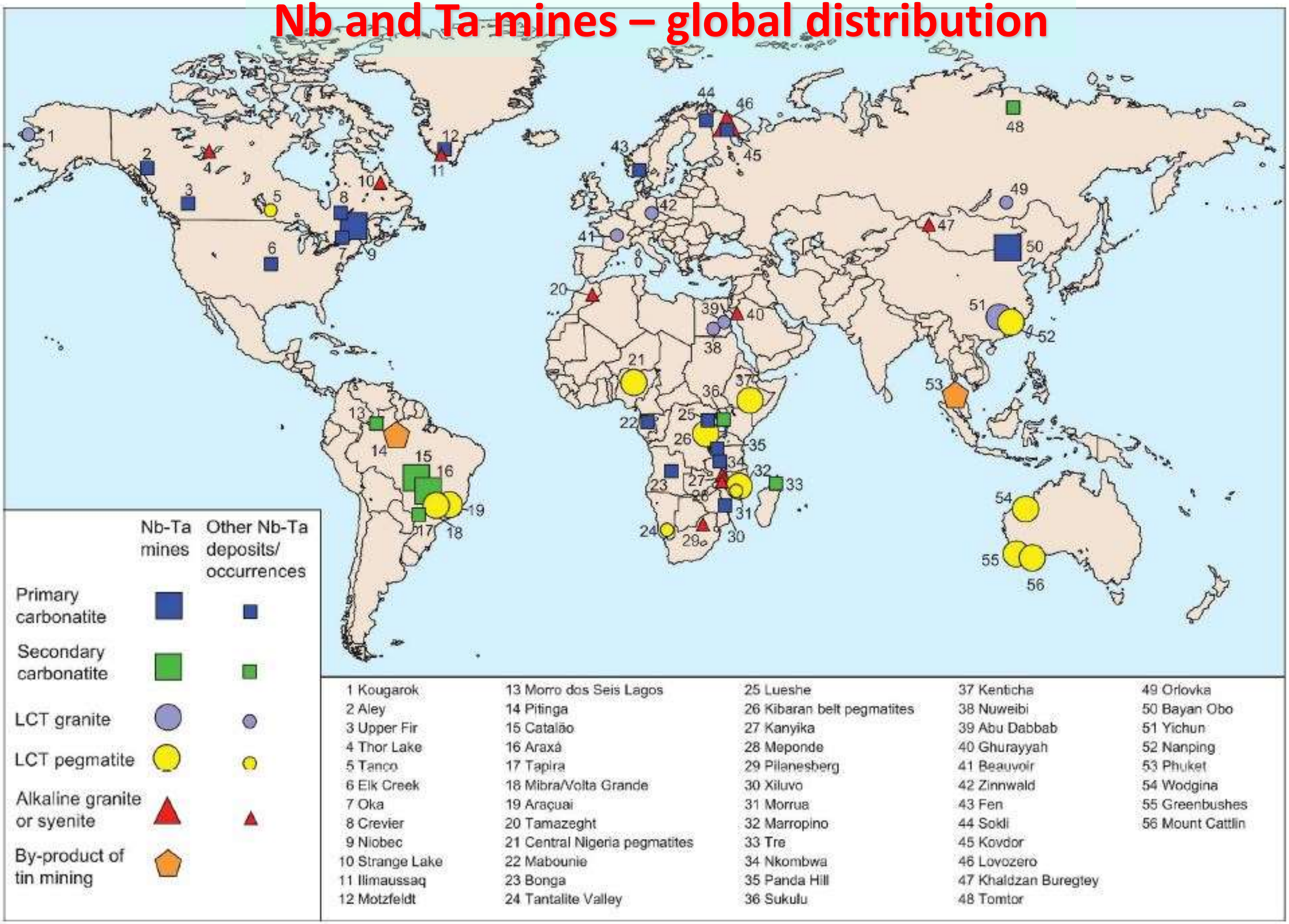
  2. **Alkaline to peralkaline granites** and **syenites** (**Nb, Y, REE, Zr, Sn, Ta**).

  3. **Peraluminous pegmatites** and **granites** (**Ta, Nb, Sn, W, Cs, Li**).

- Ta and Nb minerals are also **resistant to mechanical and chemical weathering**, and have **high specific gravities** → placer and alluvial deposits.

- A number of **Sn deposits** also contain Nb and Ta, particularly in SE Asia.

Nb and Ta mines – global distribution



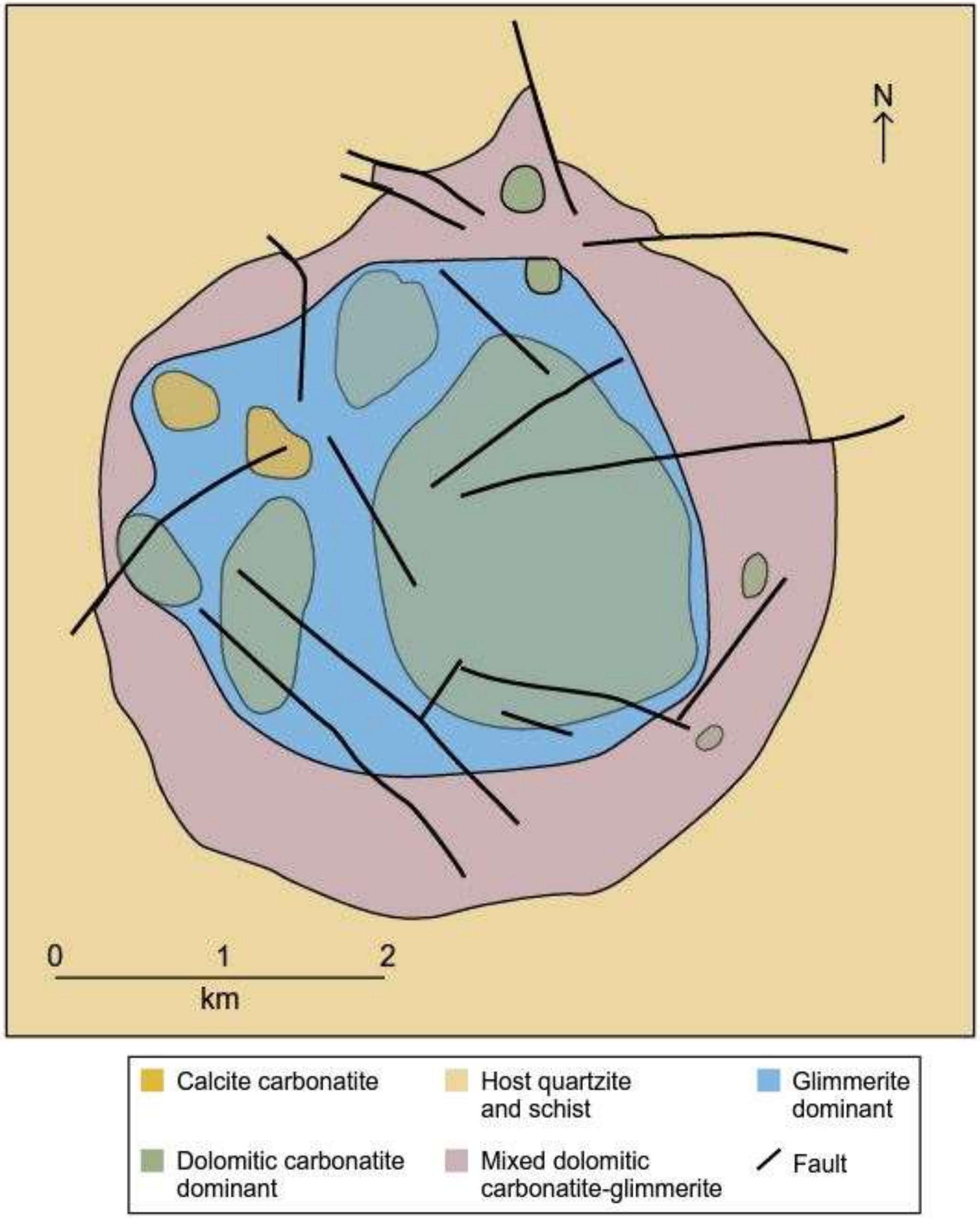
1 Kougarok
2 Aley
3 Upper Fir
4 Thor Lake
5 Tanco
6 Elk Creek
7 Oka
8 Crevier
9 Niobec
10 Strange Lake
11 Ilimaussaq
12 Motzfeldt
13 Morro dos Seis Lagos
14 Pitinga
15 Catalão
16 Araxá
17 Tapira
18 Mibra/Volta Grande
19 Araçuai
20 Tamazeght
21 Central Nigeria pegmatites
22 Mabounie
23 Bonga
24 Tantalite Valley
25 Lueshe
26 Kibaran belt pegmatites
27 Kanyika
28 Meponde
29 Pilanesberg
30 Xiluvo
31 Morrua
32 Marropino
33 Tre
34 Nkombwa
35 Panda Hill
36 Sukulu
37 Kenticha
38 Nuweibi
39 Abu Dabbab
40 Ghurayyah
41 Beauvoir
42 Zinnwald
43 Fen
44 Sokli
45 Kovdor
46 Lovozero
47 Khaldzan Buregtey
48 Tomtor
49 Orlovka
50 Bayan Obo
51 Yichun
52 Nanping
53 Phuket
54 Wodgina
55 Greenbushes
56 Mount Cattlin

Nb and Ta – carbonatite deposits

- Carbonatites are **igneous rocks** that contain **> 50% carbonate minerals**. Most carbonatites occur in **rift settings**, but it is clear that there are several different types of carbonatites, many of which are unmineralised.

- Carbonatites are **genetically related to strongly alkaline silicate rocks**, but it is not clear whether these are related by **fractional crystallization** or by **silicate-carbonatite melt immiscibility** → both are interpreted to be the product of **melting of a metasomatised mantle**.

- The most important carbonatite-hosted Nb deposits are in **Brazil** (92% of the world's Nb). E.g. **Araxá deposit ≈ 808 Mt ore**, average grade **2.3%** $\mathbf{Nb_2O_5}$.



Geology of the Araxá carbonatite complex. (Modified after Pell, 1996.)

Nb and Ta – alkaline to peralkaline granites and syenites

- Significant concentrations of Nb and Ta occur in **alkaline to peralkaline granites and syenites**. These intrusions also contain high concentrations of **Zr**, **Y** and **REE**, and generally occur in **rift** or **failed rift** tectonic settings, although there are exceptions (e.g Lovozero and Khibiny intrusions, Kola Peninsula – Russia).

- This style of mineralization has received considerable interest recently because of related **high Y and REE content**.

- One of the characteristics of this deposit type is the **wide range of Zr, Nb and REE minerals that are present** (including hydrous and anhydrous silicates, phosphates, oxide and mixed silicate-phosphate mineral phases).

- The dominant mineral of Nb and Ta is **pyrochlore**, but other complex phases such as **eudialyte** and secondary **fergusonite** are also important carriers of Nb.

- There are no current producing mines of this type, but **they are potential sources of a variety of metals in the future**.

Nb and Ta – peraluminous pegmatites

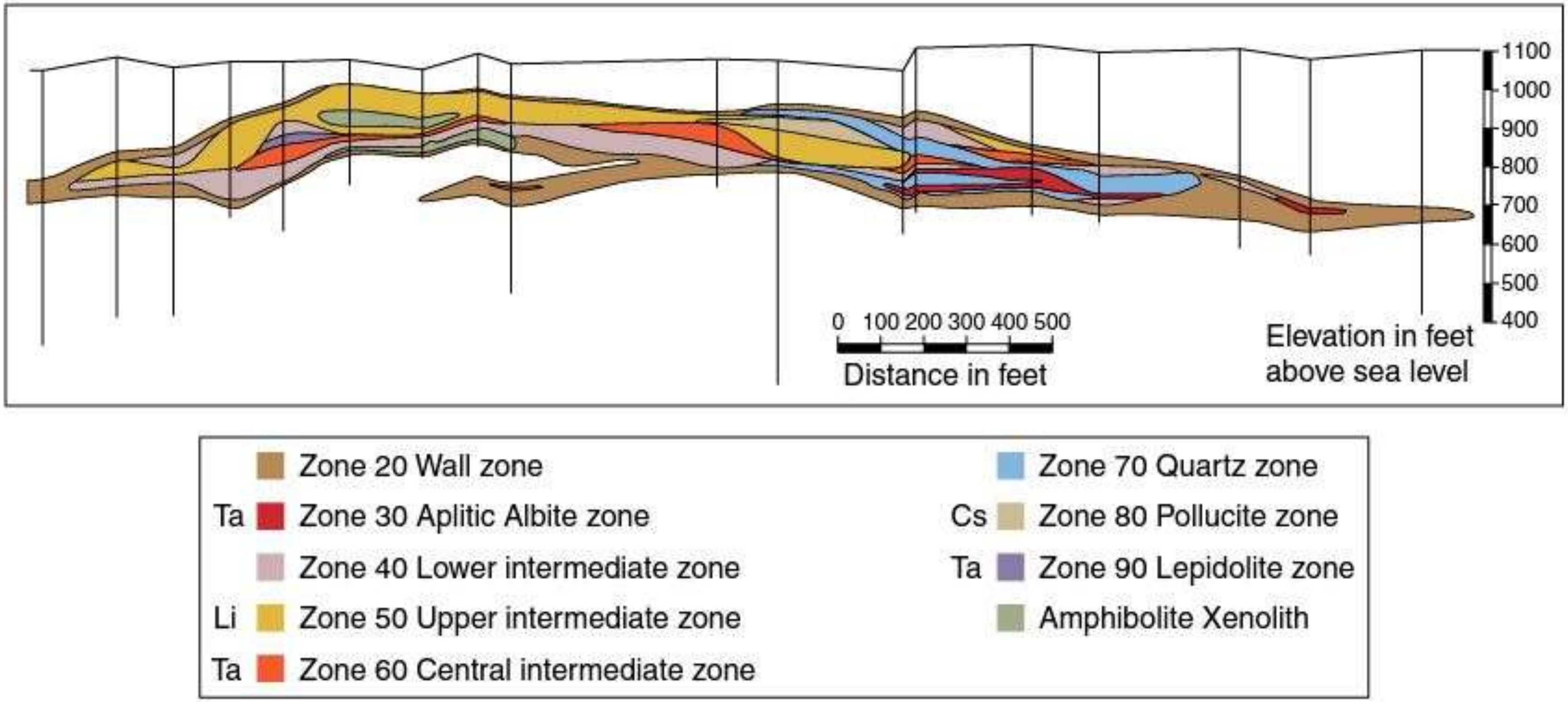


Figure 15.3 Longitudinal east–west section through the Tanco pegmatite. (Modified after Černý et al., 1996). (Cs, caesium; Li, lithium; Ta, tantalum.)

- Peraluminous pegmatites have historically been the **most important source of Ta**, and are commonly associated with **peraluminous S-type granites**, and occur as **late syn- to post-tectonic intrusions** in **collision belts**, typically in association with **shear zones**. Other elements of economic significance include **Li**, **Cs**, **Be**, **Rb**, **Nb** and **Sn**. These pegmatites are assigned to the **Li-Cs-Ta (LCT) family** of pegmatites (relatively high T and P, from 750 °C and 5 kbar to a greisen and metasomatic stage at 620 °C and 5 kbar).

Nb and Ta – peraluminous pegmatites

Figure 15.4 Banded aplite ore from the Tanco deposit. Tantalum mineralisation is contained in the banded aplite (red and blue-grey at the bottom). A massive quartz zone (dark grey) is at the top and coarse, crystalline white beryl separates the aplite and quartz. The scale is approximately 2 m across. (Courtesy of R. Linnen.)

Nb and Ta – extraction methods and processing

- **Extraction:** Ta and Nb minerals are recovered through industry-standard **open pit**, **underground** and **placer** mining methods.

- **Processing**:
  - **Pyrochlore ores** are concentrated by **flotation**, preceded by **removal of irrecoverable ultrafines** to achieve acceptable concentrate grades, generally in excess of 50% Nb_2O_5, and rejection of unwanted contaminants. Several flotation stages as well as electrical separation are required.
  - **Columbotantalite ores** almost exclusively utilize standard **wet gravity concentration** equipment.

Coltan ore

Nb – pyrochlore extraction methods and processing

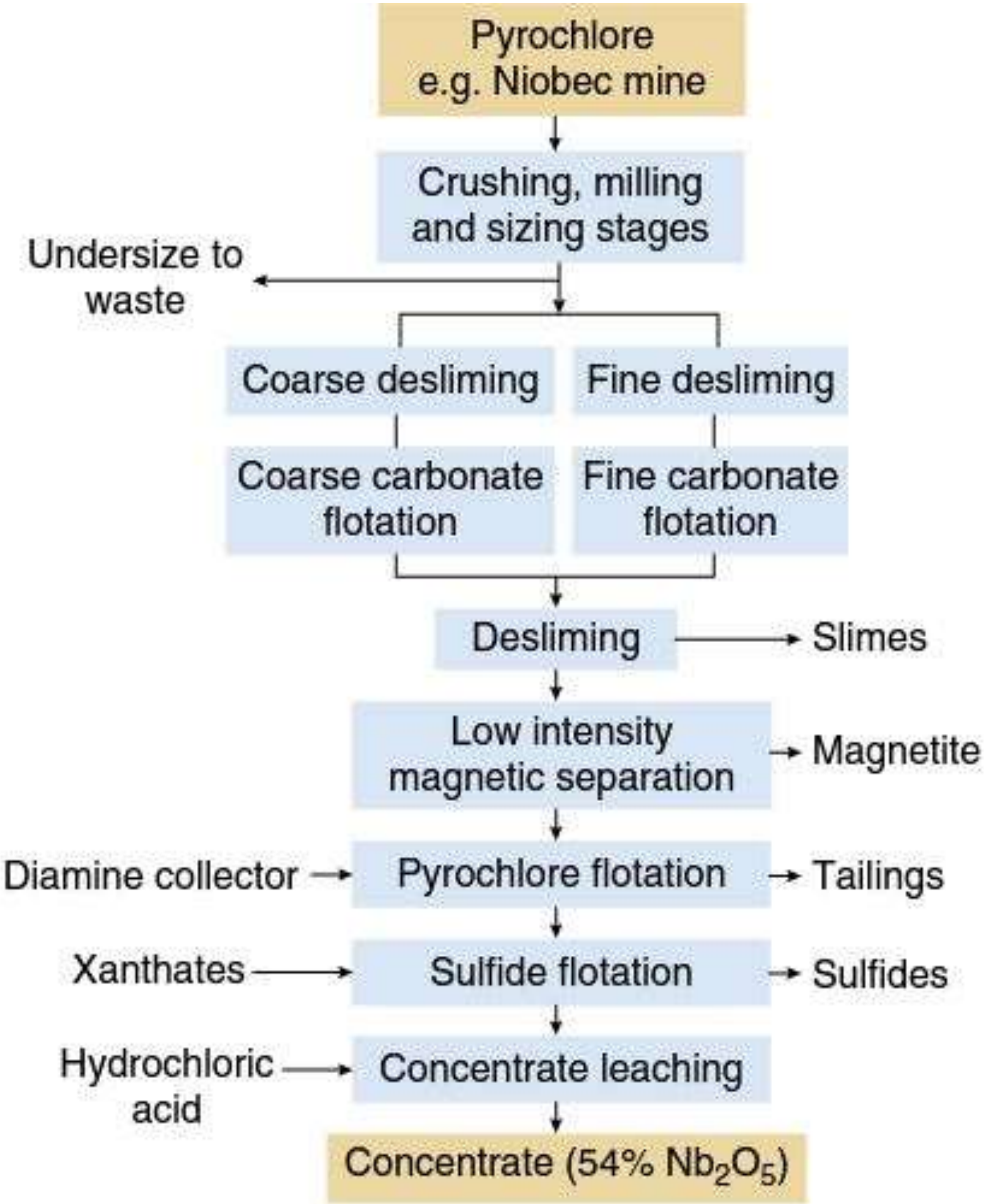
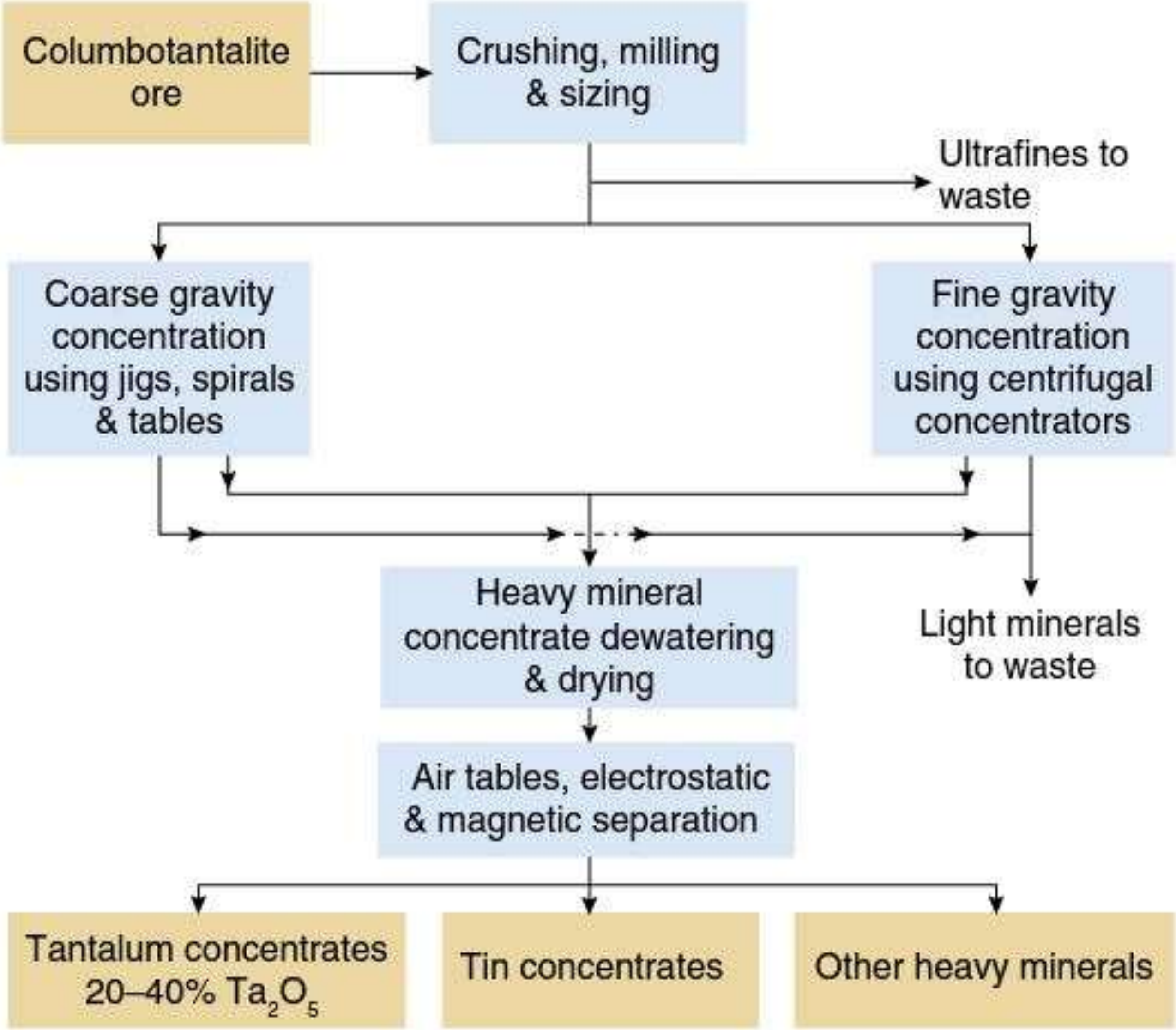


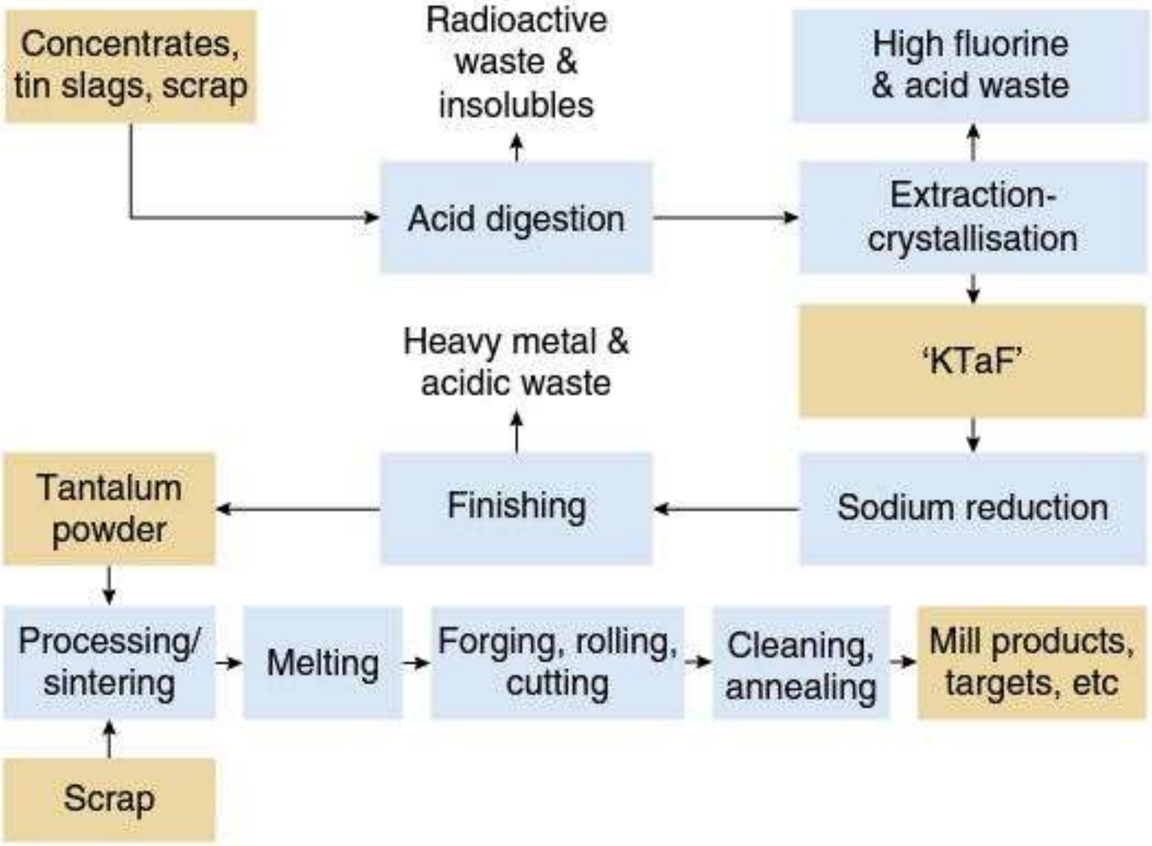
Figure 15.5 Niobium production flowsheet for the Niobec mine. (Modified after Shaw and Goodenough, 2011.)

Ta – preparation of concentrates



Schematic summary of the processes involved in the preparation of tantalum concentrates.

Ta – production of Ta from concentrates, tin slags and scrap



Concentrates, tin slags, scrap

Radioactive waste & insolubles

Acid digestion

High fluorine & acid waste

Extraction-crystallisation

'KTaF'

Heavy metal & acidic waste

Sodium reduction

Finishing

Tantalum powder

Processing/ sintering

Scrap

Melting

Forging, rolling, cutting

Cleaning, annealing

Mill products, targets, etc

Figure 15.7 Schematic flowsheet for the production of tantalum from concentrates, tin slags and scrap. ('KTaF', potassium fluortantalate).

Nb – specifications and uses

- Close to **90%** of Nb production is used to make **high-strength low-alloy steels**. The addition of Fe-Nb to steel increases strength and toughness, as well as reduces the weight.

- The **electrical resistance** of **Nb-Ti** and **Nb-Sn** alloy wire **drops to virtually zero** at or below T of liquid He (-268.8 °C) → these alloys are utilized in **superconducting magnetic coils** in **magnetic resonance imagery** (MRI), **magnetoencephalography**, **magnetic levitation** transport systems and **particle physics** experiments.

- Nb is also used for alloys and chemicals, including carbides (**Nb carbide** is used for cutting tools). **Niobium oxide** (Nb_2O_5) is used to manufacture **Li niobate** ($LiNbO_3$) for surface acoustic wave filters, camera lenses, coating on glass for PC screens and ceramic capacitors.

Ta – specifications and uses

- The first uses of Ta were **in light-bulb filaments** and **optical glasses**.
- Its widespread usage arose with the advent of the **transistors** and **solid-state avionics**. These applications continue to account for over 50% of all Ta consumption, with the most significant segment being the **Ta capacitor**, used not just in **consumer electronics**, but also in many **automobile components** (ABS, airbag activation, GPS, engine management modules).
- **Aircraft** and **medical appliances** (pacemakers, defibrillators and hearing aids),
- **Electronics**: hard-disk devices, ink-jet printer heads.
- A significant growth area is for **sputtering targets**, with Ta being used as the **diffusion barrier** between interconnects on Cu-based **semiconductors**.
- **Li tantalate** is used in **surface acoustic wave filters** (mobile phones, audio systems and TV).
- **Ta oxide** has a **high refractive index** → lenses in **mobile phones** and **high-end digital cameras**.
- **Corrosion resistant objects**, **high-T alloys** for turbines, **single-crystal alloys** (3 – 11% Ta).

Nb and Ta – recycling and substitution

- **Recycling**
  - **Nb** is recycled (≈ 20%) when **Nb-bearing steels** and **superalloys** are recycled, but scrap recovery specifically for Nb is negligible.

  - **Ta** is recycled (≈ 25%) from **electronic components** and from **Ta-bearing cemented carbide** and **superalloy scrap**.

- **Substitution**
  - As Ta prices rose in the early 2000s, **Nb** was more widely substituted into electronic capacitors (but **failed to make military specifications** in many critical end uses).

  - **Ta capacitors:** low potential for substitution. For **airbag triggers** the Ta capacitor is a must.

  - **Ta-carbide**: W (lower performance).

Nb – resources and reserves

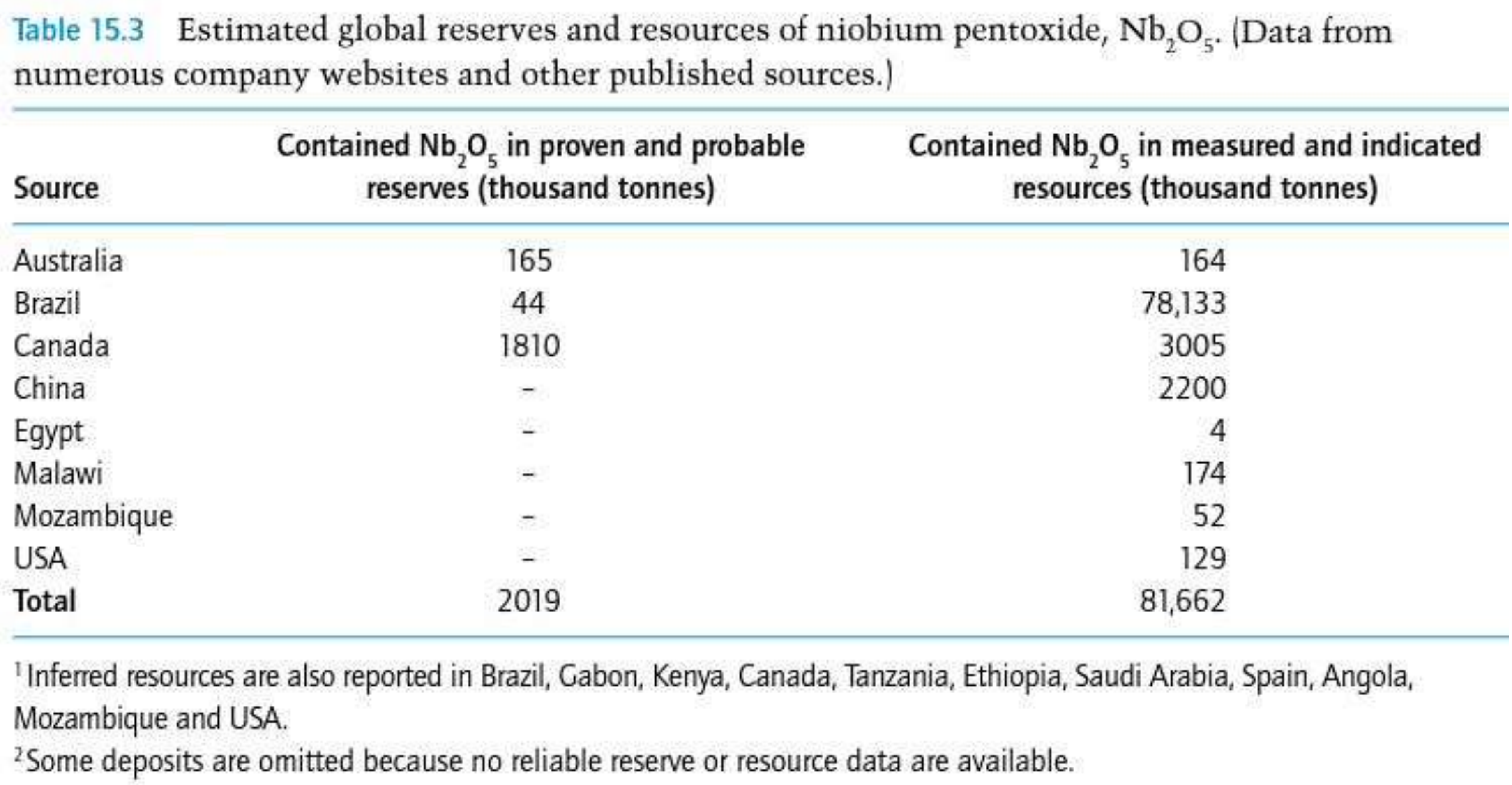


Table 15.3 Estimated global reserves and resources of niobium pentoxide, Nb_2O_5. (Data from numerous company websites and other published sources.)

Source	Contained Nb_2O_5 in proven and probable reserves (thousand tonnes)	Contained Nb_2O_5 in measured and indicated resources (thousand tonnes)
Australia	165	164
Brazil	44	78,133
Canada	1810	3005
China	–	2200
Egypt	–	4
Malawi	–	174
Mozambique	–	52
USA	–	129
Total	2019	81,662

[1] Inferred resources are also reported in Brazil, Gabon, Kenya, Canada, Tanzania, Ethiopia, Saudi Arabia, Spain, Angola, Mozambique and USA.

[2] Some deposits are omitted because no reliable reserve or resource data are available.

Ta – resources and reserves

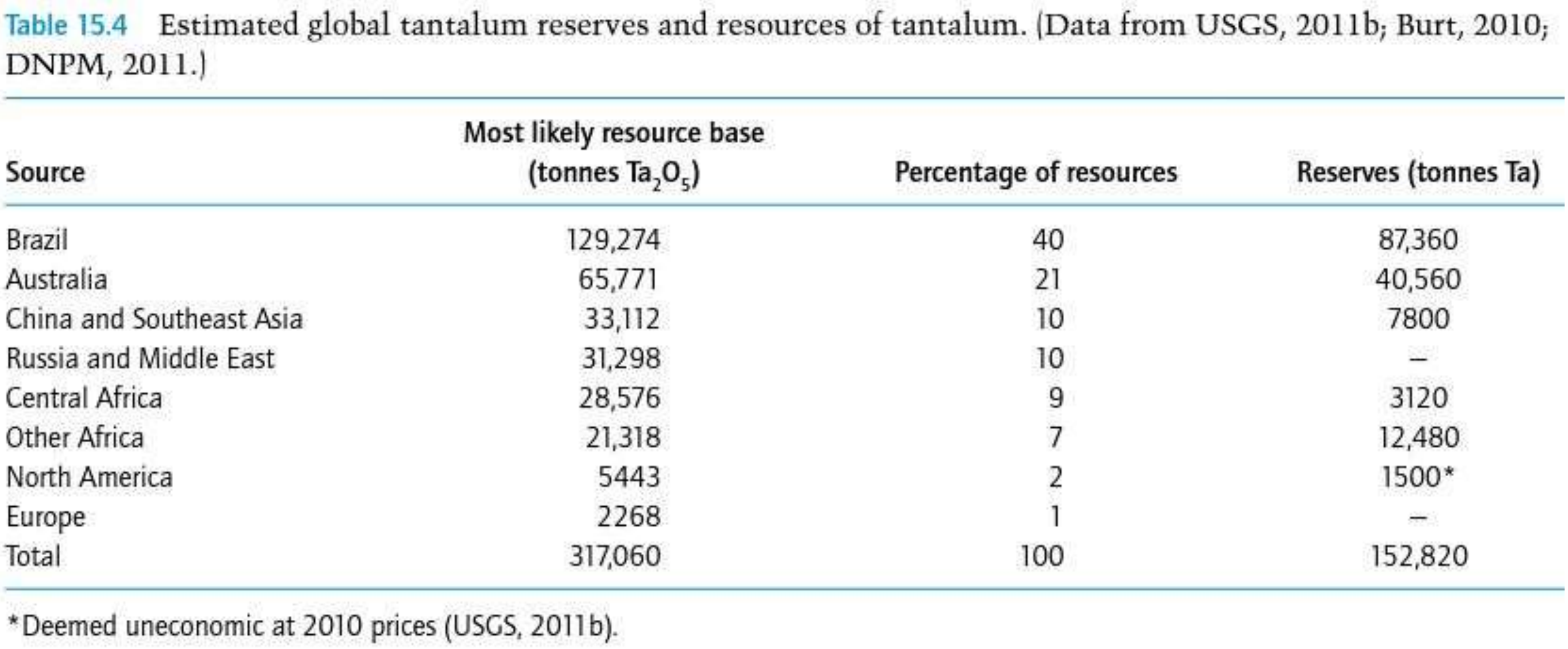


Table 15.4 Estimated global tantalum reserves and resources of tantalum. (Data from USGS, 2011b; Burt, 2010; DNPM, 2011.)

Source	Most likely resource base (tonnes Ta_2O_5)	Percentage of resources	Reserves (tonnes Ta)
Brazil	129,274	40	87,360
Australia	65,771	21	40,560
China and Southeast Asia	33,112	10	7800
Russia and Middle East	31,298	10	–
Central Africa	28,576	9	3120
Other Africa	21,318	7	12,480
North America	5443	2	1500*
Europe	2268	1	–
Total	317,060	100	152,820

*Deemed uneconomic at 2010 prices (USGS, 2011b).

Nb – production

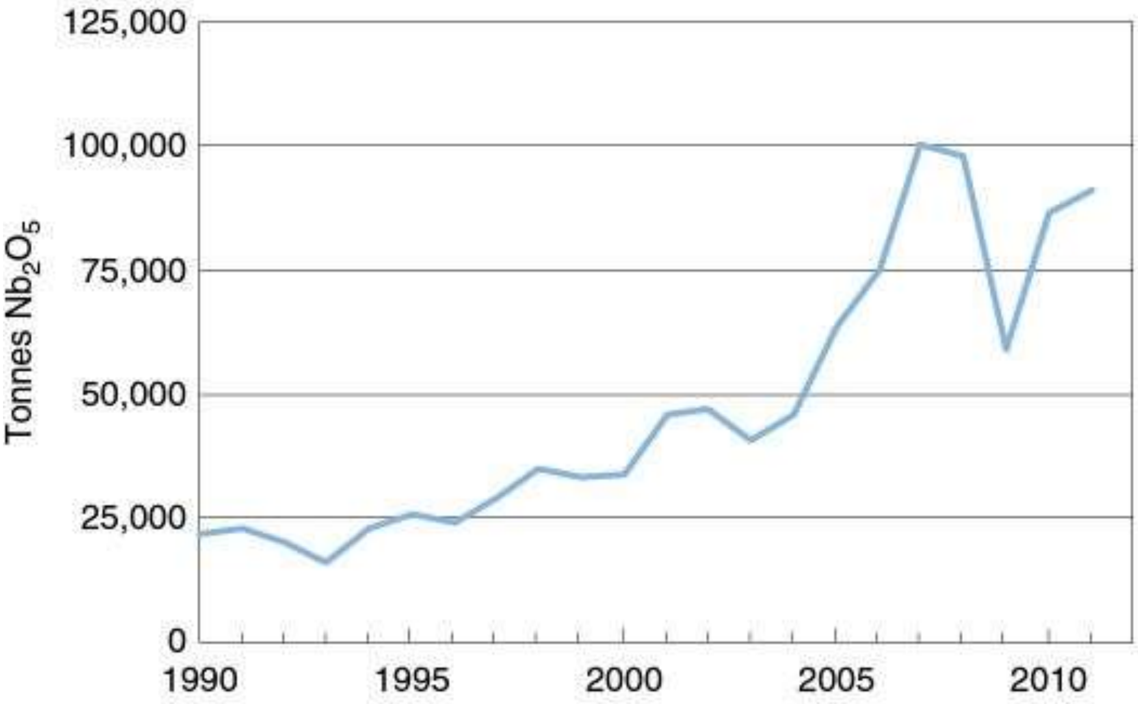


Figure 15.9 Global niobium production, 1990–2011. (After Schwela, 2011, with additional data from T.I.C. Bulletins.)

Ta – production

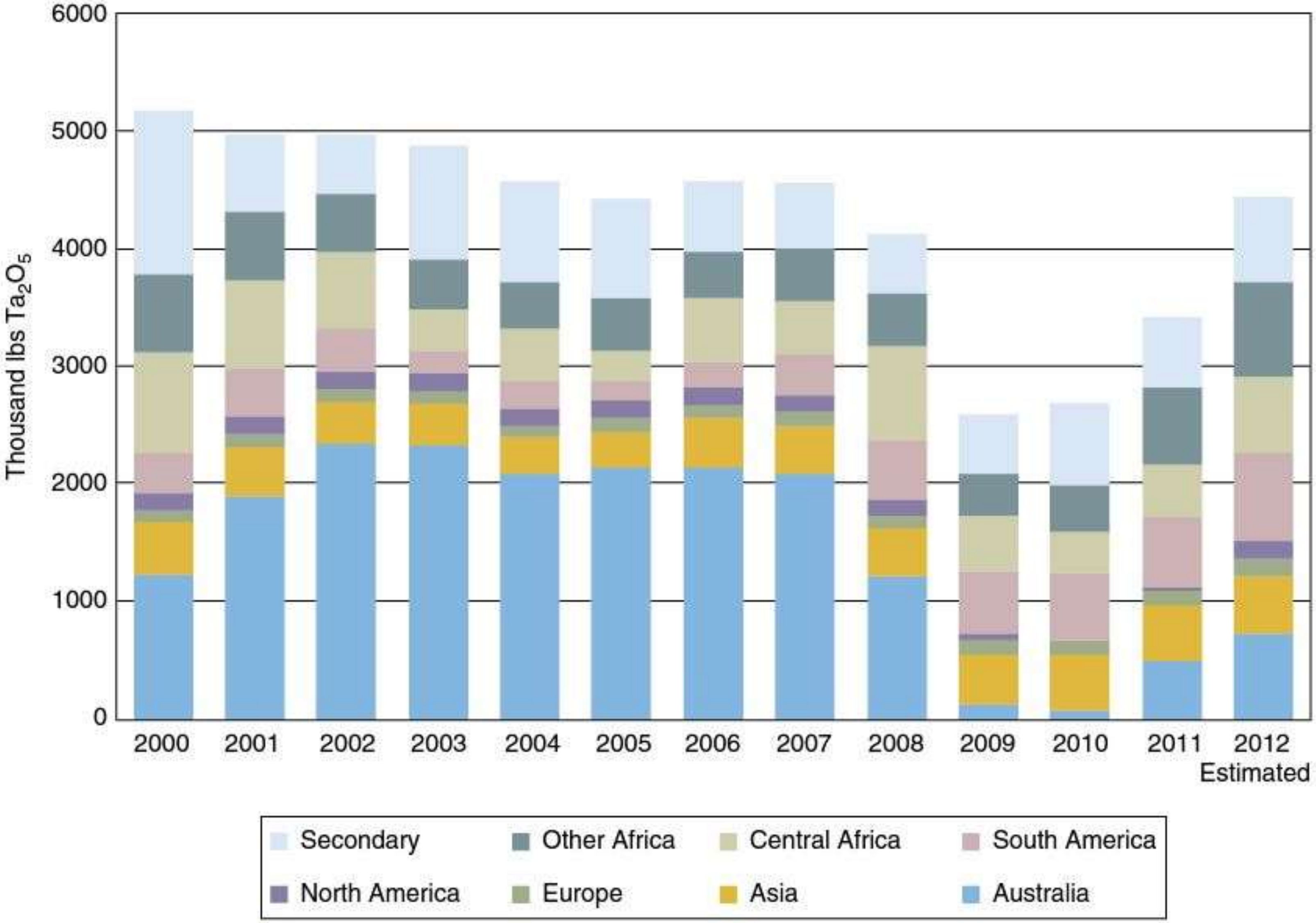


Figure 15.10 Global production of tantalum from concentrates and tin slags, 2000–2012. (Data from various trade documents, government statistics, and industry sources and estimates.) The 'Secondary' category includes low-grade tin slags and shipments of old stocks from the US Defence Logistics Agency 'stockpile'.

Nb and Ta – prices

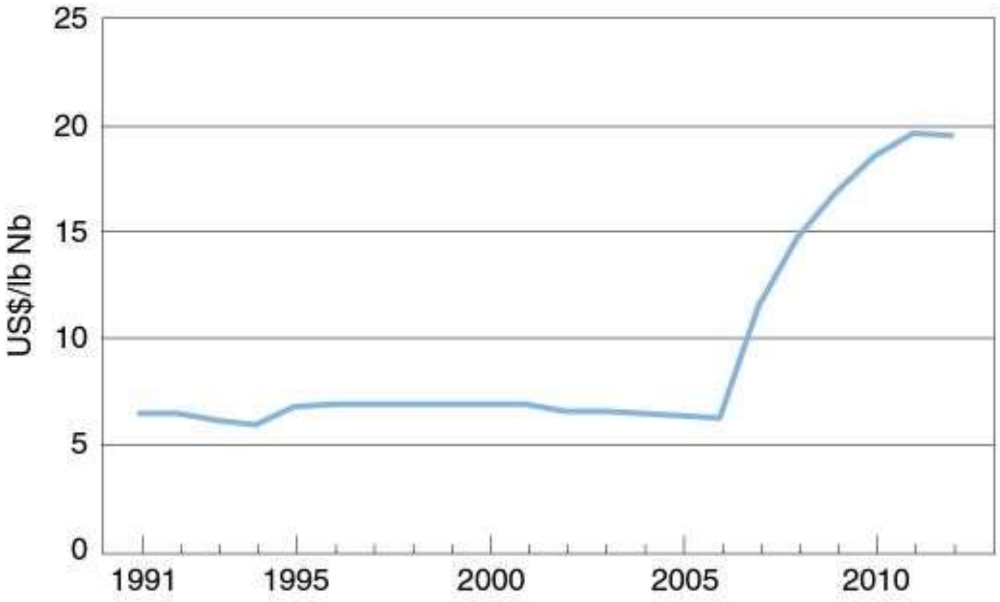


Figure 15.11 Average annual ferroniobium price per pound of contained niobium, 1991–2012. (Based upon various technical and commercial sources.)

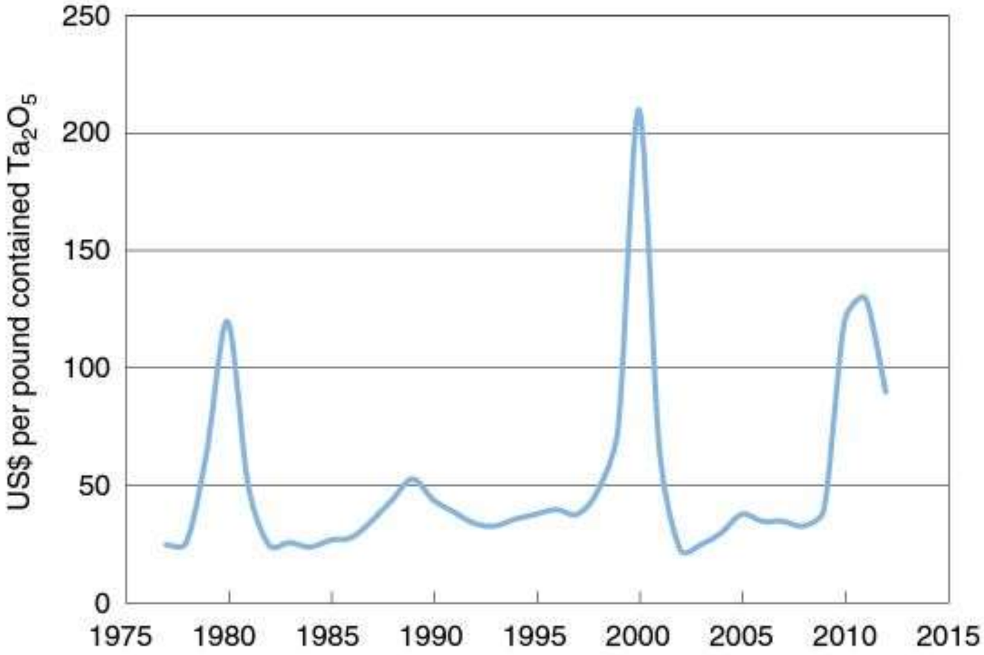


Figure 15.12 Average annual price for tantalum pentoxide contained in 30% tantalum pentoxide (Ta_2O_5) concentrate, 1977–2012. (Based upon various technical and commercial sources.)

Nb and Ta – environmental issues

- **Nb and Ta ores do not pose any special environmental problems** (lack of sulfides).

- **Ta concentrates** produced from **pegmatites** generally contain minute quantities of natural **U** and **Th**. Next-generation concentrates (**alkaline** and **peralkaline deposits**) will almost certainly have **higher levels of these radioactive elements**.

- The **pyrochlore concentrates** used to produce Fe-Nb also contain **Th** and **U**.

- The **solid forms** of **Nb** and **Ta** do not pose special environmental problems (powders can be irritant → Ta capacitors).

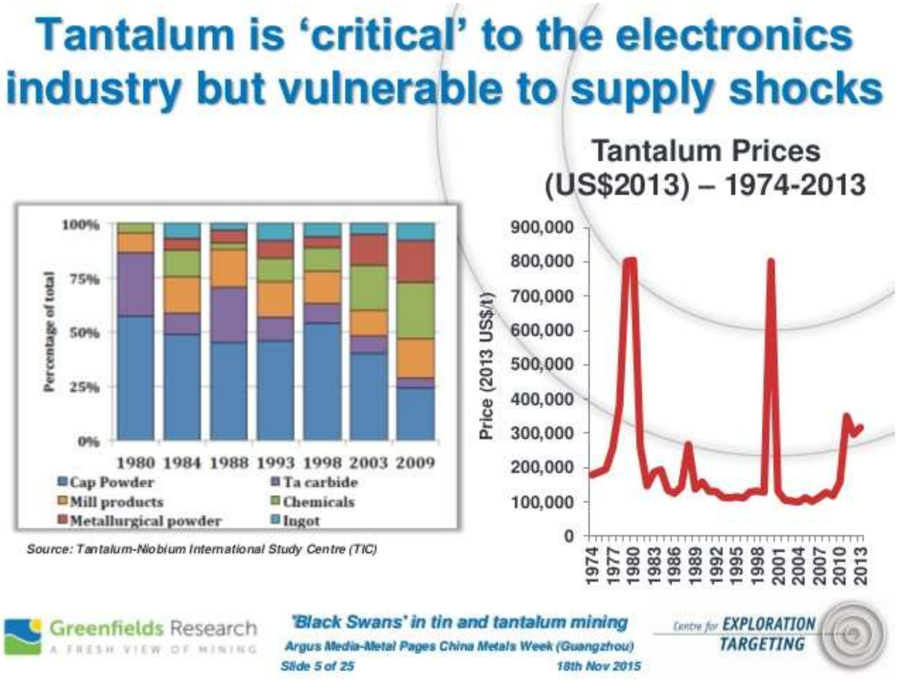
Nb and Ta – outlook

- The **known global resources of Nb are exceptionally large**. More problematic, however, is a lack of suppliers (e.g. policies of Brazil).

- A major use of **Nb** is in **steel** and **other alloys** essential to the development of infrastructure (railways, pipelines and automobiles).

- The role of Nb and its utility in **electronics** is still in the early stages of development. It now finds its way into **computer chips** and **superconductors** for **medical technologies**.

- **Ta**: the **capacitor** marked has declined, while in other sectors it has increased. It will remain a **critical component in electronic uses**.



Tantalum is 'critical' to the electronics industry but vulnerable to supply shocks

Tantalum Prices (US$2013) – 1974-2013

Source: Tantalum-Niobium International Study Centre (TIC)

'Black Swans' in tin and tantalum mining

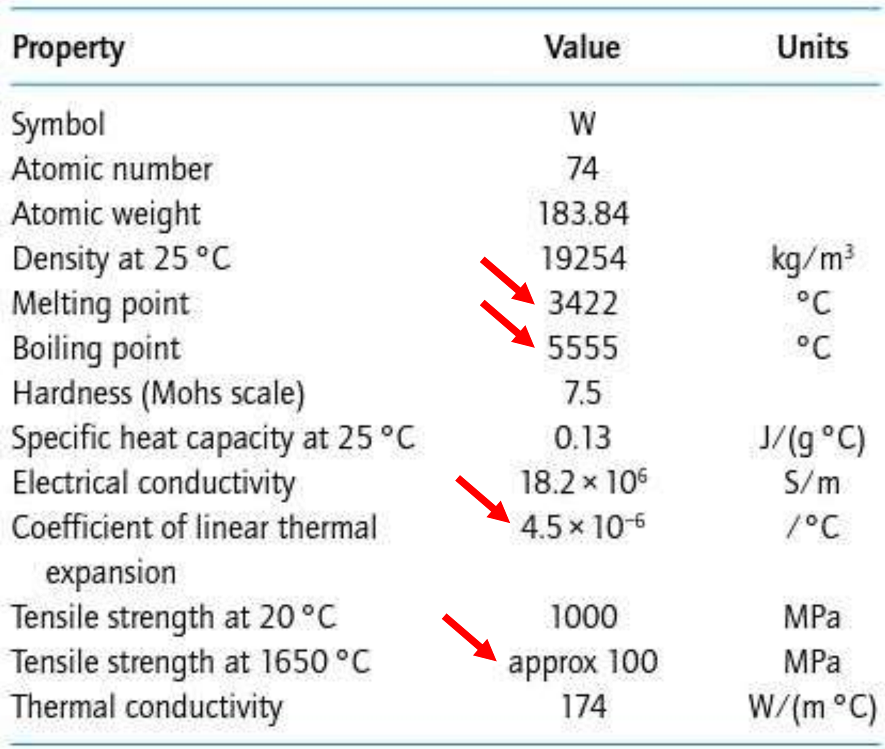
Argus Media-Metal Pages China Metals Week (Guangzhou)

Slide 5 of 25

18th Nov 2015

Tungsten

W – definitions and characteristics

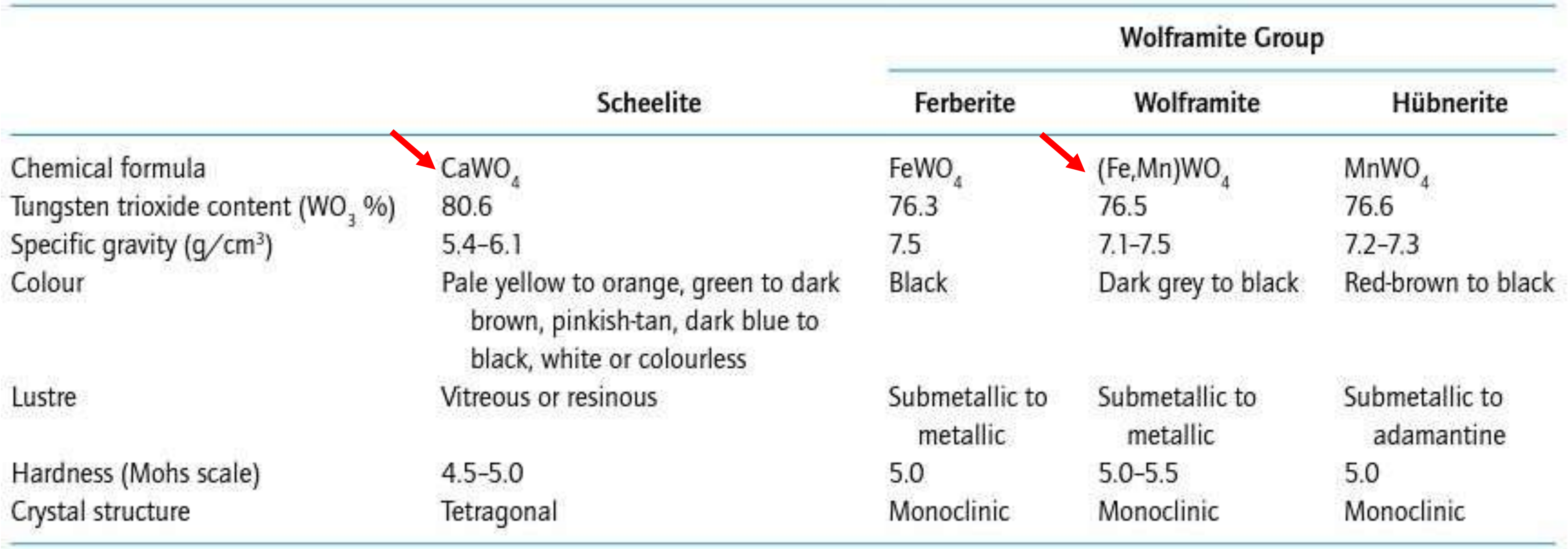


Property	Value	Units
Symbol	W	
Atomic number	74	
Atomic weight	183.84	
Density at 25 °C	19254	kg/m^3
Melting point	3422	°C
Boiling point	5555	°C
Hardness (Mohs scale)	7.5	
Specific heat capacity at 25 °C	0.13	J/(g °C)
Electrical conductivity	18.2×10^6	S/m
Coefficient of linear thermal expansion	4.5×10^{-6}	/°C
Tensile strength at 20 °C	1000	MPa
Tensile strength at 1650 °C	approx 100	MPa
Thermal conductivity	174	W/(m °C)

- **Tungsten**, also known as **wolfram**, was discovered in **1781** when Carl Wilhelm Scheele, produced tungstic acid from **scheelite**.
- The name tungsten comes from the Nordic words "*tung*" and "*sten*", meaning "heavy" and "stone". The name "*wolfram*" has older roots, and is believed to have been used because the yield of Sn during smelting was reduced if W minerals were present.
- The main applications of W are in "**hard metals**", i.e. **W carbide** and **cemented carbides**, used for cutting, drilling and cemented carbides.

- W is a **hard**, **very dense**, steel-grey to greyish-white metal. It has the **highest melting point** of all non-alloyed metals and the second highest of all elements behind C. Of all pure metals, W has the **lowest coefficient of expansion** and the **highest tensile strength** at **T>1650 °C**.
- W is also known for its **high density** (similar to Au), **high thermal and electrical conductivities**, **excellent corrosion resistance**, does not react with air and water at room T and is largely **unaffected by most acids**.

W – abundance in the Earth and mineralogy



			Wolframite Group	
	Scheelite	**Ferberite**	**Wolframite**	**Hübnerite**
Chemical formula	$CaWO_4$	$FeWO_4$	$(Fe,Mn)WO_4$	$MnWO_4$
Tungsten trioxide content (WO_3 %)	80.6	76.3	76.5	76.6
Specific gravity (g/cm^3)	5.4–6.1	7.5	7.1–7.5	7.2–7.3
Colour	Pale yellow to orange, green to dark brown, pinkish-tan, dark blue to black, white or colourless	Black	Dark grey to black	Red-brown to black
Lustre	Vitreous or resinous	Submetallic to metallic	Submetallic to metallic	Submetallic to adamantine
Hardness (Mohs scale)	4.5–5.0	5.0	5.0–5.5	5.0
Crystal structure	Tetragonal	Monoclinic	Monoclinic	Monoclinic

- Average abundance of W in the Earth's continental crust ≈ **1 ppm**. The **upper crust** contains ≈ **1.9 ppm** W, whereas the middle and lower ≈ **0.6 ppm**. The abundance of W in the **oceans** is ≈ **0.1 ppb**. The average concentration in **workable ores** is usually between **0.1 – 1.0 % WO_3**.

- W does not occur in nature as a free metal. Only **scheelite** (blue-white fluorescence in UV light) and **wolframite** group minerals are abundant enough to be considered ores. Secondary W minerals, such as hydrotungstite $H_2WO_4 \cdot H_2O$ can be produced by alteration processes or weathering and may cause problems during processing.

Scheelite

Wolframite

Mineralienkabinett (c) MZ 1999 http://www.gimizu.de

W – major deposit classes

- W deposits usually occur within, or near to, **orogenic belts** resulting from **subduction-related plate tectonics**. All major deposits types are associated with **granitic intrusions** or with **medium-** to **high –grade metamorphic rocks**. Werner et al. (1998) classified major W deposits into seven types:

1. **Vein/stockwork**
2. **Skarn**
3. **Disseminated or greisen deposits**
4. **Porphyry**
5. **Stratabound**
6. **Placer**
7. **Brine/evaporite.**

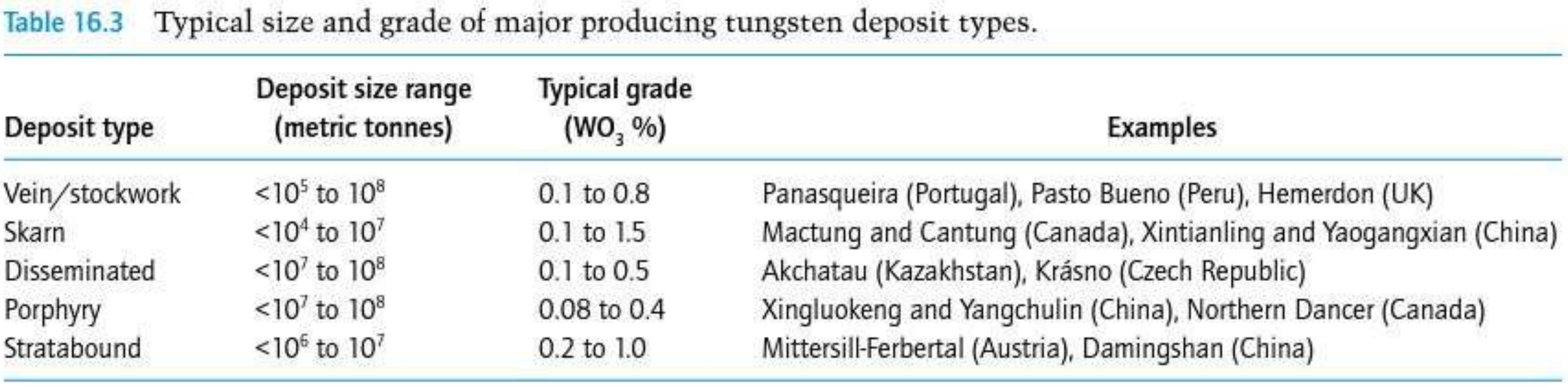
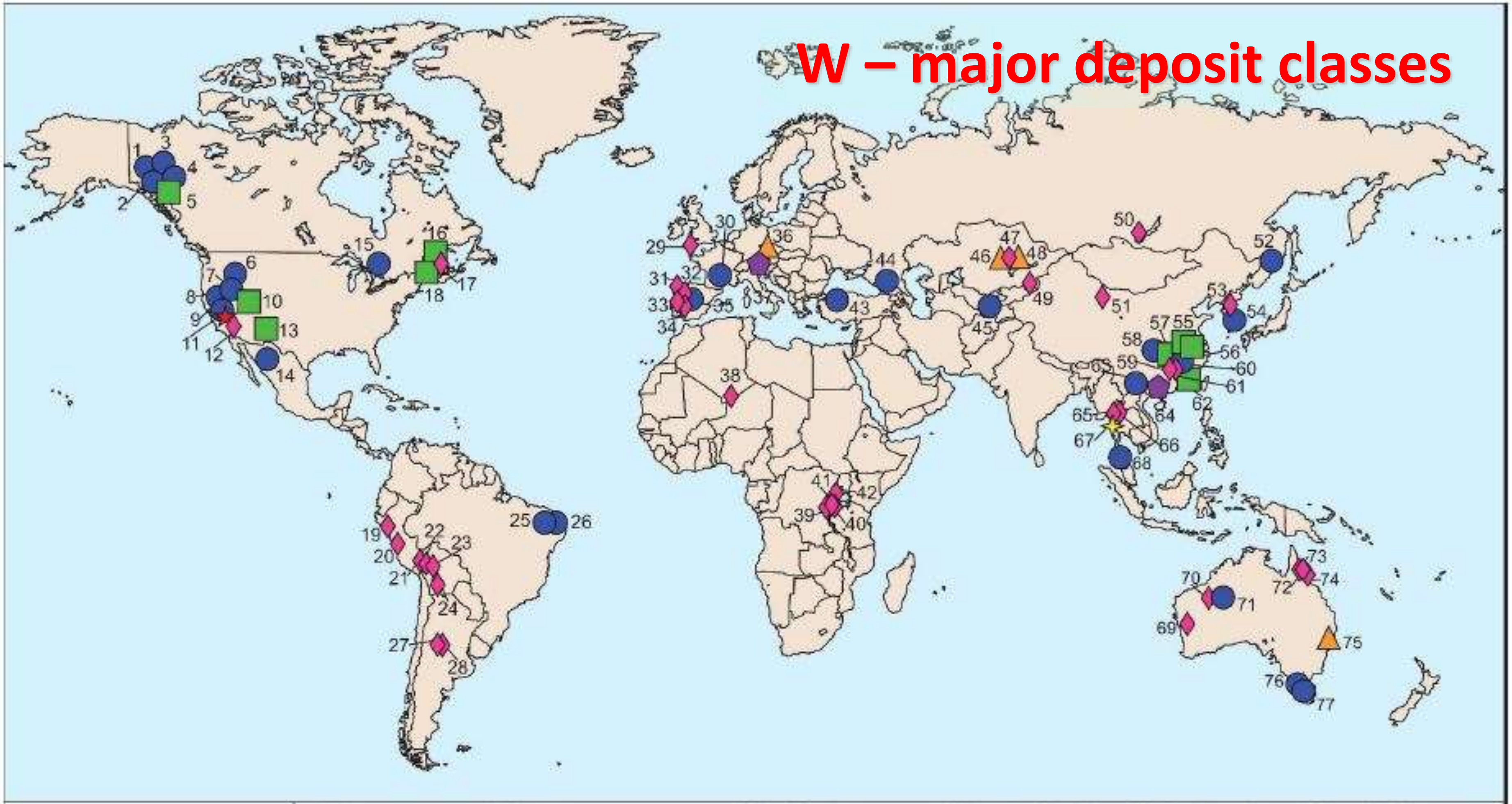


Table 16.3 Typical size and grade of major producing tungsten deposit types.

Deposit type	Deposit size range (metric tonnes)	Typical grade (WO_3 %)	Examples
Vein/stockwork	$<10^5$ to 10^8	0.1 to 0.8	Panasqueira (Portugal), Pasto Bueno (Peru), Hemerdon (UK)
Skarn	$<10^4$ to 10^7	0.1 to 1.5	Mactung and Cantung (Canada), Xintianling and Yaogangxian (China)
Disseminated	$<10^7$ to 10^8	0.1 to 0.5	Akchatau (Kazakhstan), Krásno (Czech Republic)
Porphyry	$<10^7$ to 10^8	0.08 to 0.4	Xingluokeng and Yangchulin (China), Northern Dancer (Canada)
Stratabound	$<10^6$ to 10^7	0.2 to 1.0	Mittersill-Ferbertal (Austria), Damingshan (China)

W – major deposit classes



Brine/Evaporite	★
Disseminated	▲
Placer	✦
Porphyry	🟩
Skarn	●
Stratabound	⬟
Vein/Stockwork	◆

1 Mar
2 Risby
3 Mactung
4 Cantung
5 Northern Dancer
6 Brown's Lake
7 Indian Springs
8 Mill City District
9 Pine Creek
10 Climax
11 Searles Lake
12 Andrew
13 Victorio
14 Naica
15 Fostung
16 Sisson Brook
17 Burnt Hill
18 Mount Pleasant
19 Pasto Bueno
20 Morococha/San Cristobal
21 Palca Once
22 Bolsa Negra
23 Chicote Grande
24 Tazna
25 Bodó
26 Currais Novos / Barra Verde / Boca de Lage
27 Los Avestruces
28 Los Condores
29 Hemerdon
30 Furnade
31 Santa Comba
32 Barruecopardo
33 Panasqueira
34 La Parrilla
35 Los Santos
36 Krásno
37 Mittersill-Ferbertal
38 Laouni
39 Idjwi
40 Nyakabingo
41 Gifurwe
42 Nyamuliro/Bjordal
43 Uludag
44 Tyrnyauz
45 Maykhura
46 Kara Oba
47 Verkhne-Kayrakty
48 Akchatau
49 Boguty
50 Dzhida District
51 Ta'ergou
52 Vostok-2
53 Gogsan Mannjon
54 Sangdong
55 Yangchuling
56 Xingluokeng/ Xianglushan
57 Shizhuyuan
58 Xintianling
59 Xihuashan
60 Yaogangxian
61 Nanling district
62 Lianhuashan
63 Bai Sha Po
64 Damingshan
65 Mae Lama
66 Doi Ngom
67 Heinze Basin
68 Khao Soon
69 Mount Mulgine
70 Cookes Creek/Big Hill
71 O'Callaghans
72 Wolfram Camp
73 Mount Carbine
74 Watershed
75 Torrington
76 King Island
77 Kara

W – major deposit classes

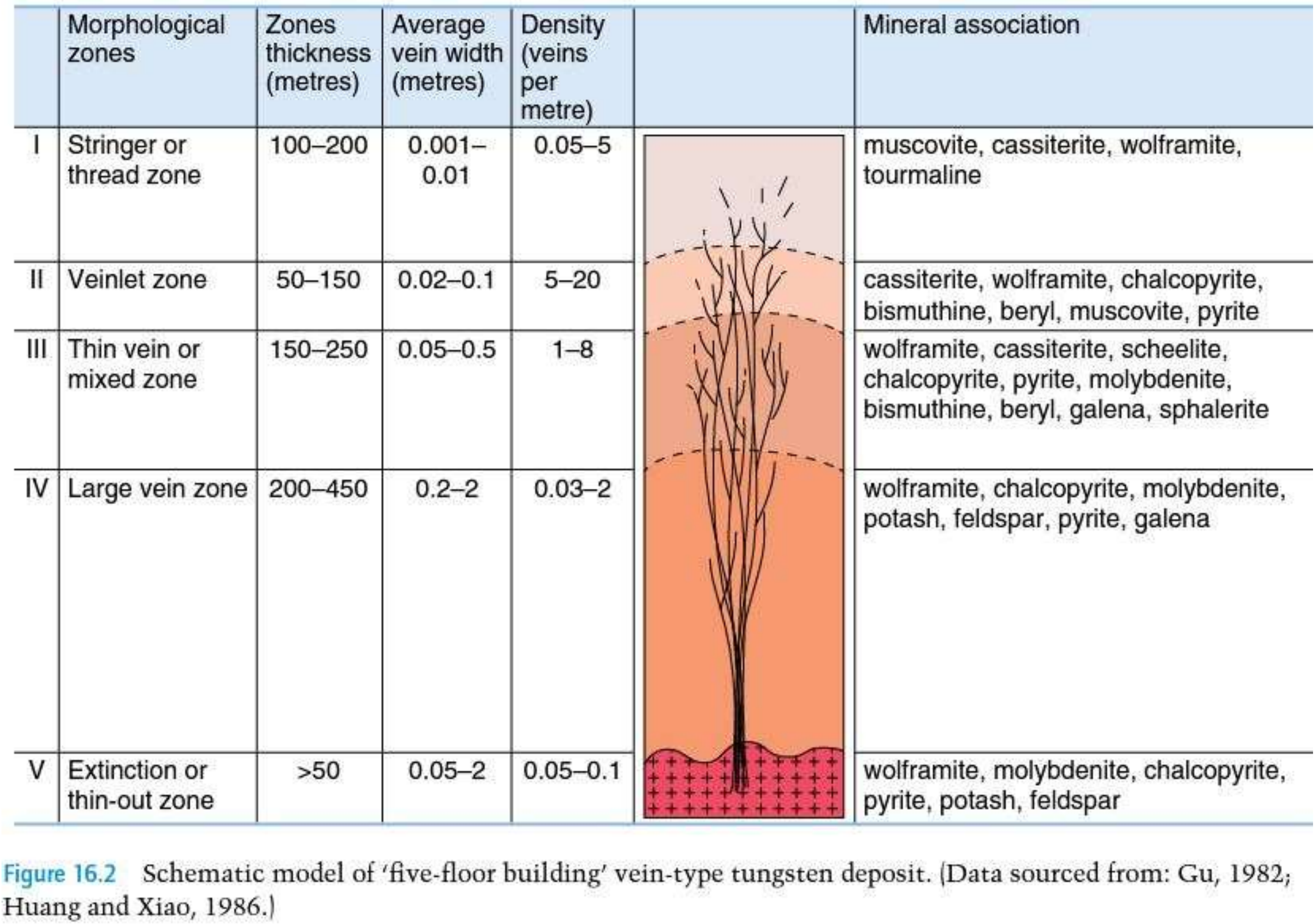
- **Vein and stockwork deposits**: genetically related to the development of **fractures** that occur in or near **granitic intrusions** during **emplacement** and **crystallization**. These fissures are frequently filled with **quartz** and can be up to several meters in width. The veining is commonly bordered by **greisen**, and the mineralogy of vein deposits range from the simple **Qtz + wolframite**, to the complex (> 50 vein-forming minerals, containing Sn, Cu, Mo, Bi, Au, U, Th, REE and phosphates).

- **Skarn deposits**: skarns are coarse-grained rocks dominated by **calc-silicate minerals** that have formed by **metasomatic processes** in sequences containing **carbonate-bearing rocks**. Most are found adjacent to **plutons**, but they can also occur along faults, major shear zones and shallow geothermal systems. **Scheelite $CaWO_4$** is the principal W mineral and this may occur as disseminated grains or fracture filling.

- **Disseminated or greisen deposits**: **wolframite or scheelite** are disseminated in **highly altered (greisenised) granite or granitic pegmatite**. They usually occur near to the upper parts that are emplaced at depths of between **0.5 and 5 km**, where fluids can **boil** but are **prevented from escaping** to the surface.

- **Porphyry deposits**: **extensive**, **low-grade** deposits formed following the **separation of metal-rich fluids** from a crystallizing wet magma. W (wolframite or scheelite) tends to concentrate in **stockwork zones**.

Vein-type W deposits



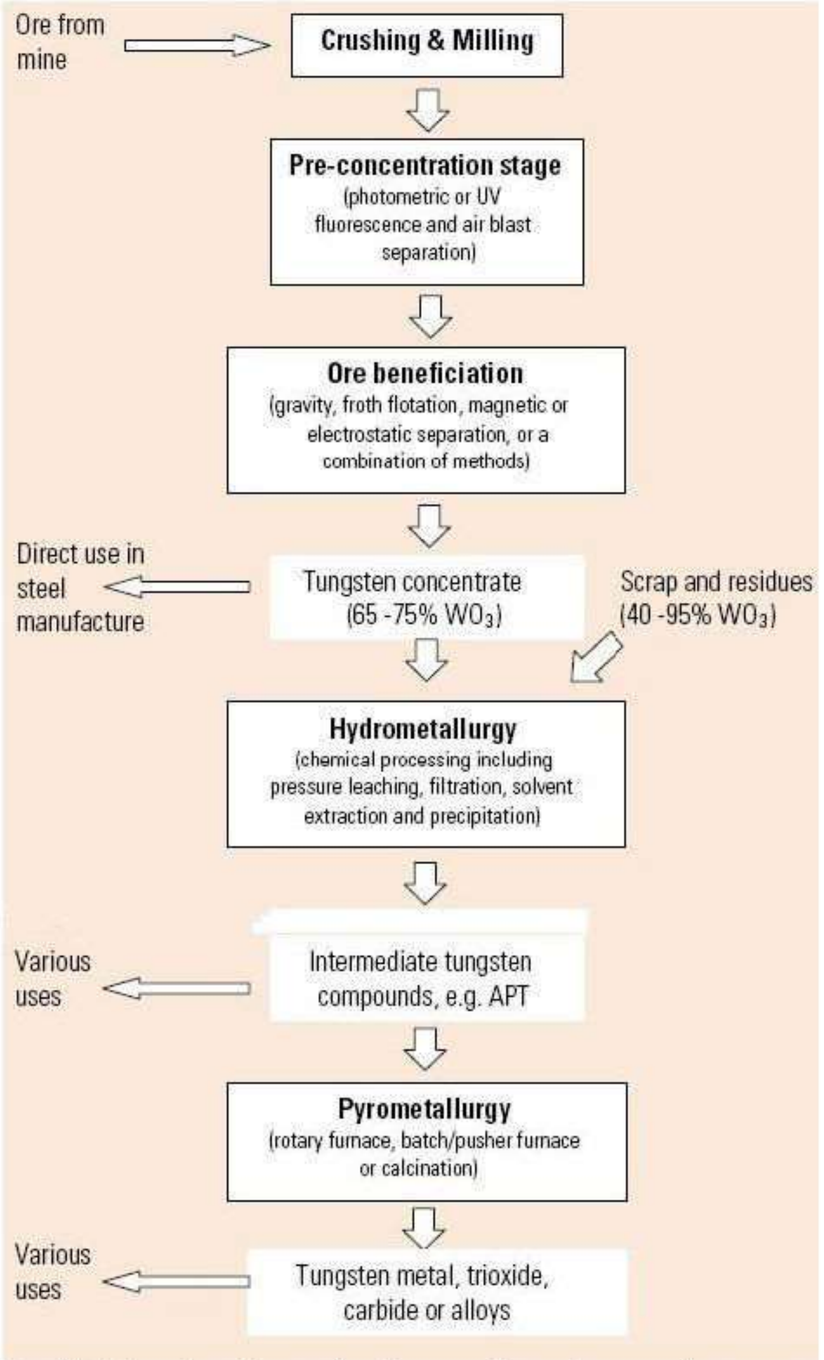
	Morphological zones	Zones thickness (metres)	Average vein width (metres)	Density (veins per metre)		Mineral association
I	Stringer or thread zone	100–200	0.001–0.01	0.05–5		muscovite, cassiterite, wolframite, tourmaline
II	Veinlet zone	50–150	0.02–0.1	5–20		cassiterite, wolframite, chalcopyrite, bismuthine, beryl, muscovite, pyrite
III	Thin vein or mixed zone	150–250	0.05–0.5	1–8		wolframite, cassiterite, scheelite, chalcopyrite, pyrite, molybdenite, bismuthine, beryl, galena, sphalerite
IV	Large vein zone	200–450	0.2–2	0.03–2		wolframite, chalcopyrite, molybdenite, potash, feldspar, pyrite, galena
V	Extinction or thin-out zone	>50	0.05–2	0.05–0.1		wolframite, molybdenite, chalcopyrite, pyrite, potash, feldspar

Figure 16.2 Schematic model of 'five-floor building' vein-type tungsten deposit. (Data sourced from: Gu, 1982; Huang and Xiao, 1986.)

W – extraction methods and processing

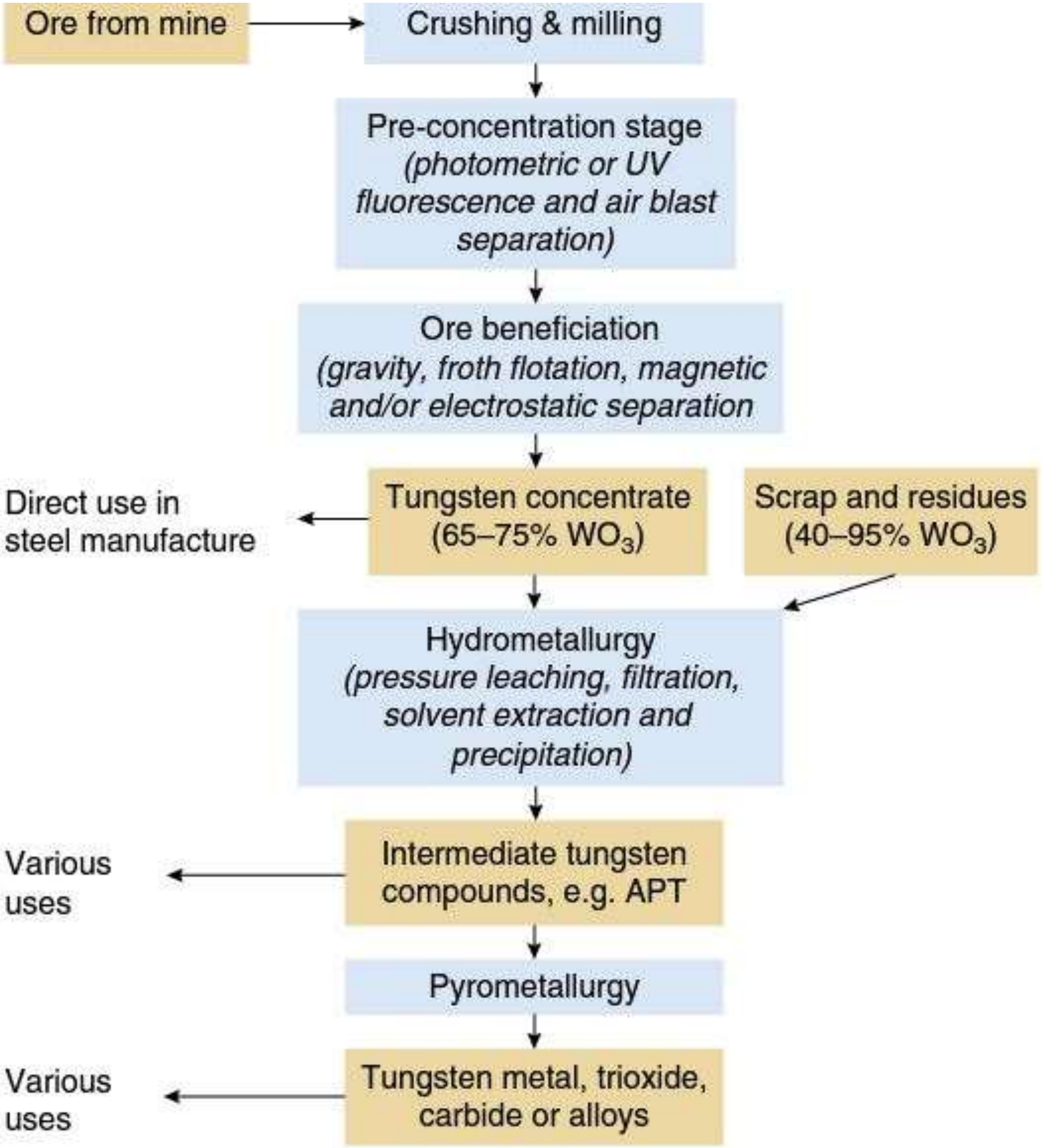
- **Extraction:** most W is mined from **sub-surface (underground) mines**.

- **Processing**: the first phase of processing the ore is beneficiation at the mine site to **increase the W content**. The resulting concentrate containing **> 65% WO$_3$** can either be used directly for production of **ferro-tungsten** and **steel** manufacture, converted to a number of intermediate W compounds (e.g. ammonium paratungstate, APT) by hydrometallurgical processes or further refined to pure W using pyrometallurgical techniques (the calcination under oxidizing condition converts APT to W trioxide).



Simplified flow chart illustrating the general steps in processing tungsten.
(Source: British Geological Survey—tungsten.)

W – processing



Ore from mine

Crushing & milling

Pre-concentration stage *(photometric or UV fluorescence and air blast separation)*

Ore beneficiation *(gravity, froth flotation, magnetic and/or electrostatic separation*

Direct use in steel manufacture

Tungsten concentrate (65–75% WO_3)

Scrap and residues (40–95% WO_3)

Hydrometallurgy *(pressure leaching, filtration, solvent extraction and precipitation)*

Various uses

Intermediate tungsten compounds, e.g. APT

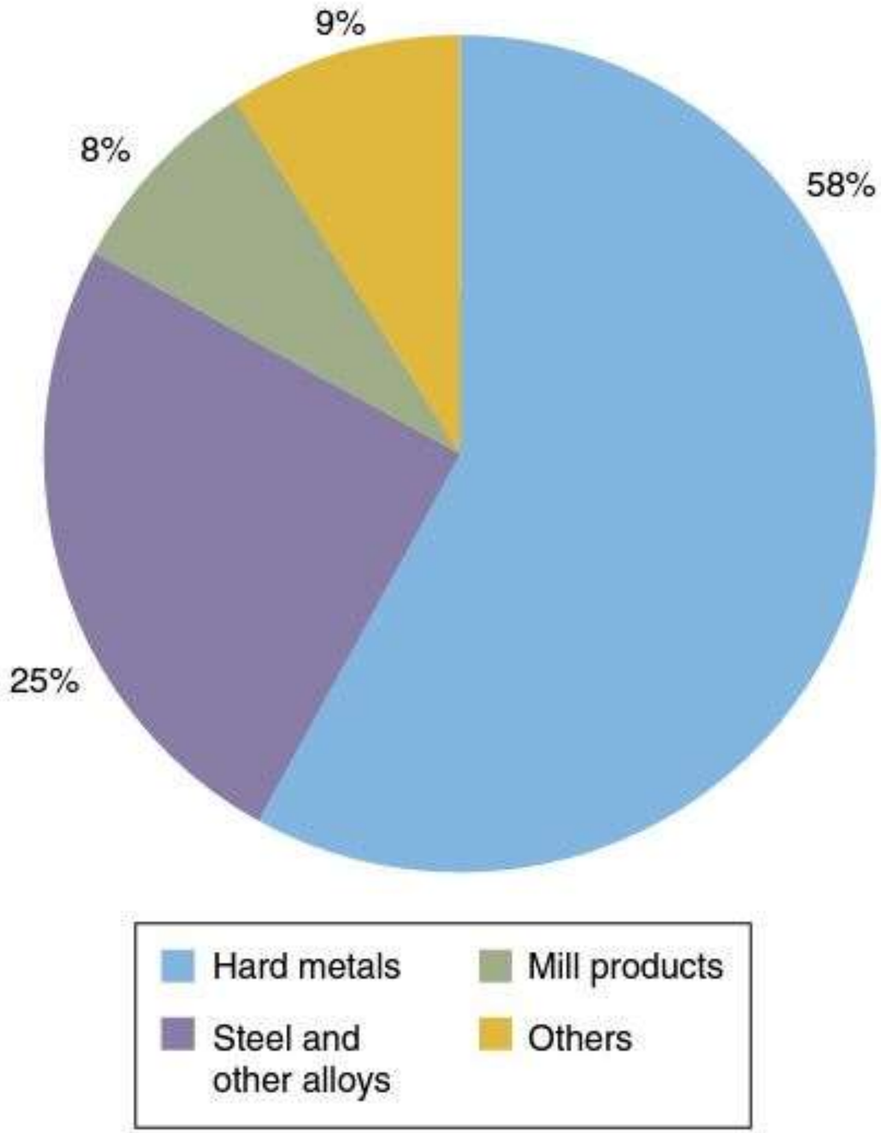
Pyrometallurgy

Various uses

Tungsten metal, trioxide, carbide or alloys

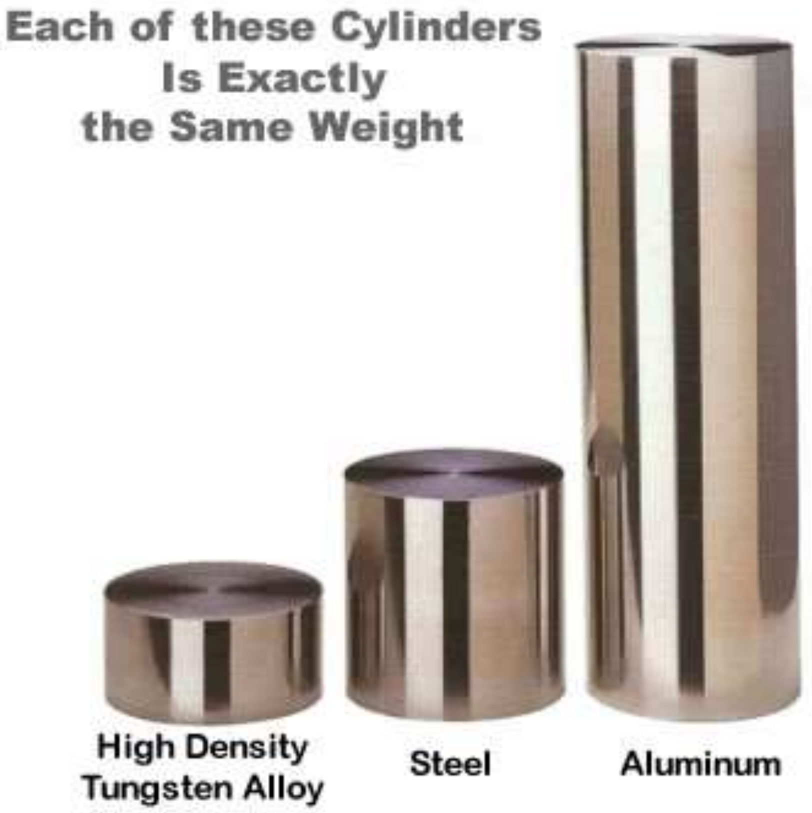
Figure 16.3 Simplified flow diagram illustrating the generic steps in processing tungsten.

W – specifications and uses



- **Ammonium paratungstate (APT)**: $(NH_4)_{10}(W_{12}O_{41})\cdot 5H_2O$ is the main W raw material traded in the market, usually calcined to yellow trioxide (WO_3) or blue oxide ($W_{20}O_{58}$).
- **Ammonium metatungstate (AMT)**: $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ is a highly soluble white crystalline powder. Produced from APT in an electrolytic cell.
- **Tungsten trioxide (WO_3)**
- **Tungsten blue oxide (TBO) $WO_{2.97}$**
- **Tungsten metal powder**: produced from yellow or blue W oxide in hydrogen reduction furnaces.
- **Tungsten heavy-metal-alloy (WHAs)**: W alloy that typically contain 90 – 98% wt. W in combination with a mix of Ni, Fe, Cu and/or Co.
- **Tungsten carbide (WC) and semi-carbide (W_2C)**: produced by the reaction of W metal powder with pure C powder at 900 – 2200 °C (carburization). High melting point (2870 °C) and extremely hard.

W – specifications and properties



- **Ferrotungsten (FeW and Fe_2W)**: remarkably robust alloy, high melting point. By combining **Fe** with **W**, the brittleness of metallic W is much reduced.

- **Non-ferrous tungsten alloys**: composites with **Cu**, **Ag**, **Ni** and rare metals. Hard, heat-resistant materials, superior wear resistance, robust physical properties at high T.

- **Superalloys**: usually with **Ni**, **Co** or **Fe-Ni**. Excellent mechanical strength and creep resistance at high T

PROPERTIES OF W

- **Very high melting point**
- **Very high density**
- **Extreme strength**
- **High wear resistance**
- **High tensile strength**
- **Low coefficient of expansion**
- **High thermal and electrical conductivity**

W – uses

- **Hard metals**: **W carbides** and **cemented carbides** (W carbides and Co, or Ti, Ta, Nb) → cutting, drilling, wear-resistant parts or coatings. Important in **metal-working** (40%), **mining** (30%) and **petroleum** (20%) industries.

- **Steel and other alloys**: high-speed steel (HSS), heat-resistant steel and tool steel.

- **Superalloys**: aerospace, industrial gas turbines and marine turbine industries (e.g flue-gas desulfurization, heat exchangers, industrial furnaces, jet-engine combustion chambers).

- **Mill products (wire, sheets or rods)**: ideal for **electrical** and **electronic applications** (e.g. bulb filaments, discharge lightning electrodes, vacuum tubes, heating elements, medical X-ray tubes, automotive ignition systems), welding electrodes (TIG).

- **Chemical and other applications**:
  - APT → colouring agent in porcelain industry or catalysts
  - AMT → reagent for chemical analysis and corrosion inhibitor
  - WF_6 → semiconductor circuits (200 t/year)

W – recycling and substitution

- **Recycling**: **more than 30%** of total world's supply is from recycled sources.
  - **Old scrap** (cemented carbide parts, W and W alloys, old superalloy scrap, W-bearing catalysts)
  - **New scrap**: generated during the processing of W concentrates.
  - **Unrecovered scrap**: chemical applications (except catalysts), wear of cemented carbide parts, erosion of electrical contacts.
  - **Recycling methods**: metallurgical and hydrometallurgical techniques.

- **Substitution**
  - Limited options for substitution in many applications (especially **high-T**).
  - **Mill products:** Mo.
  - **W steels**: Mo.
  - **Bulb filaments**: fluorescent lamps and LEDs.
  - **Weights and armor-piercing projectiles**: depleted U.

W – resources, reserves and production

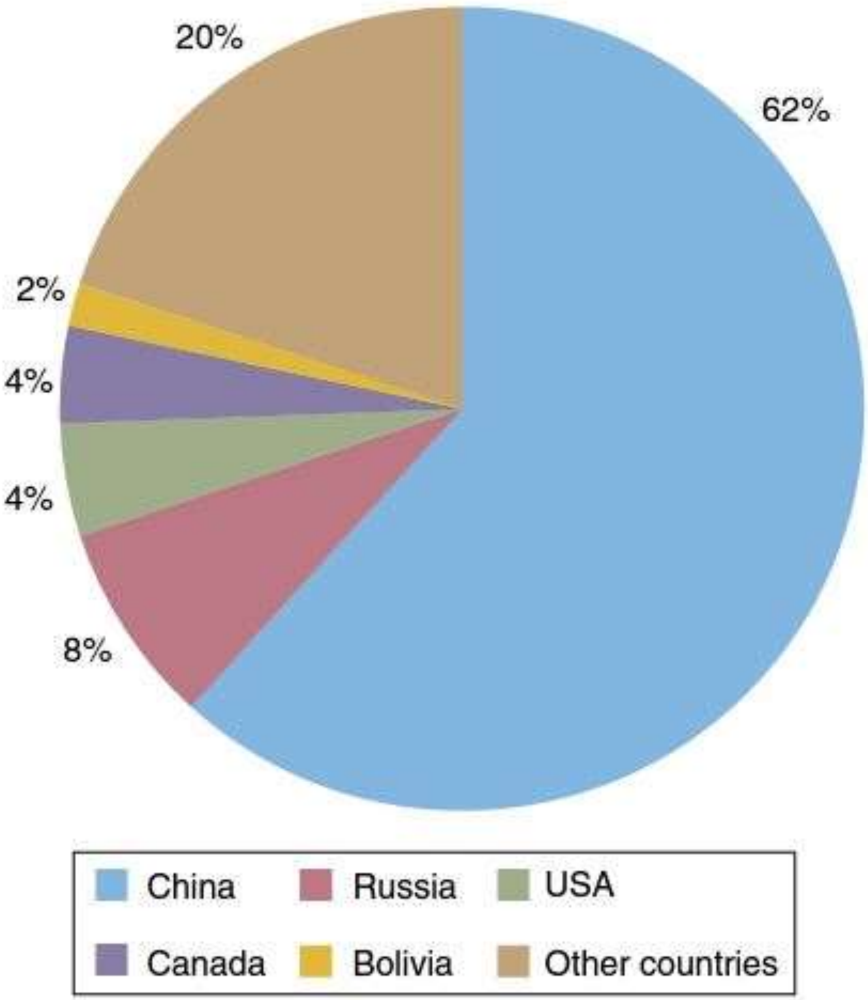


Figure 16.5 Location of the estimated world reserves of tungsten, as at December 2011 (Shedd, 2012a).

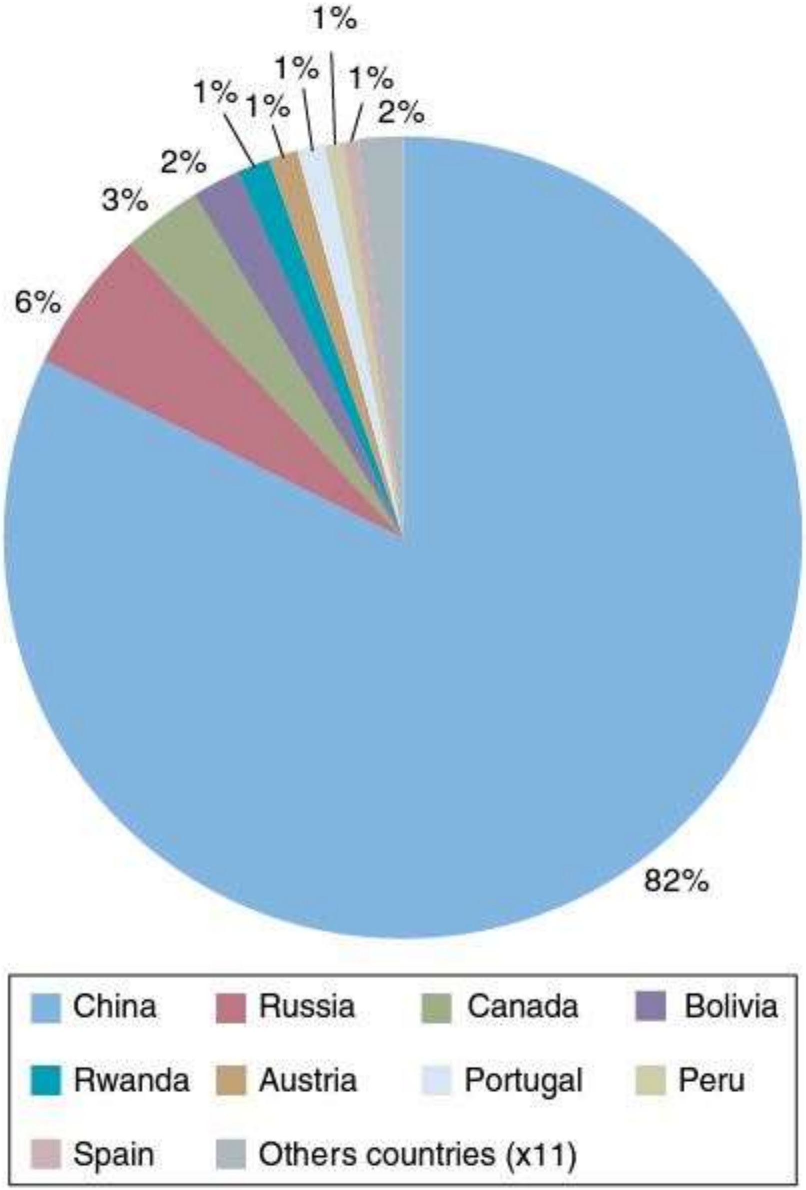


Figure 16.7 Mine production of tungsten in 2011. (Data from British Geological Survey, 2013.)

W – production

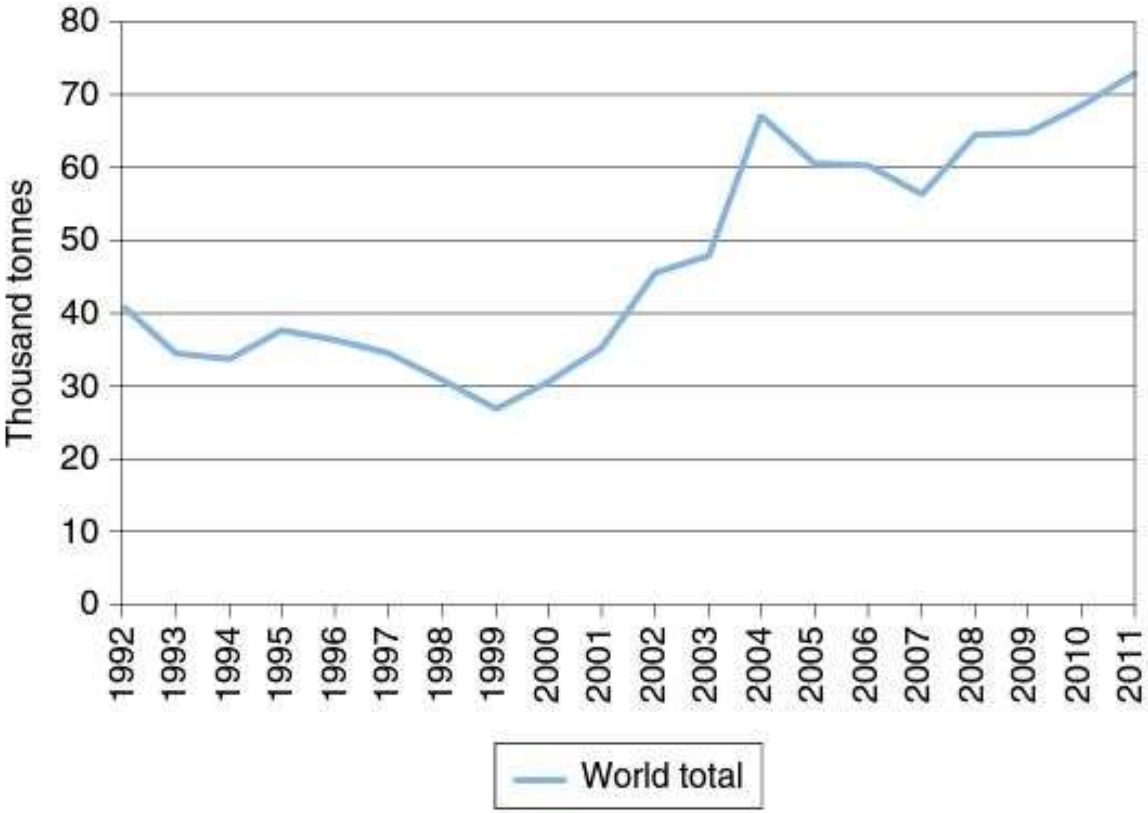


Figure 16.6 Mine production of tungsten, 1992–2011. (Data from British Geological Survey World Mineral Statistics database.)

W – evolution of W production

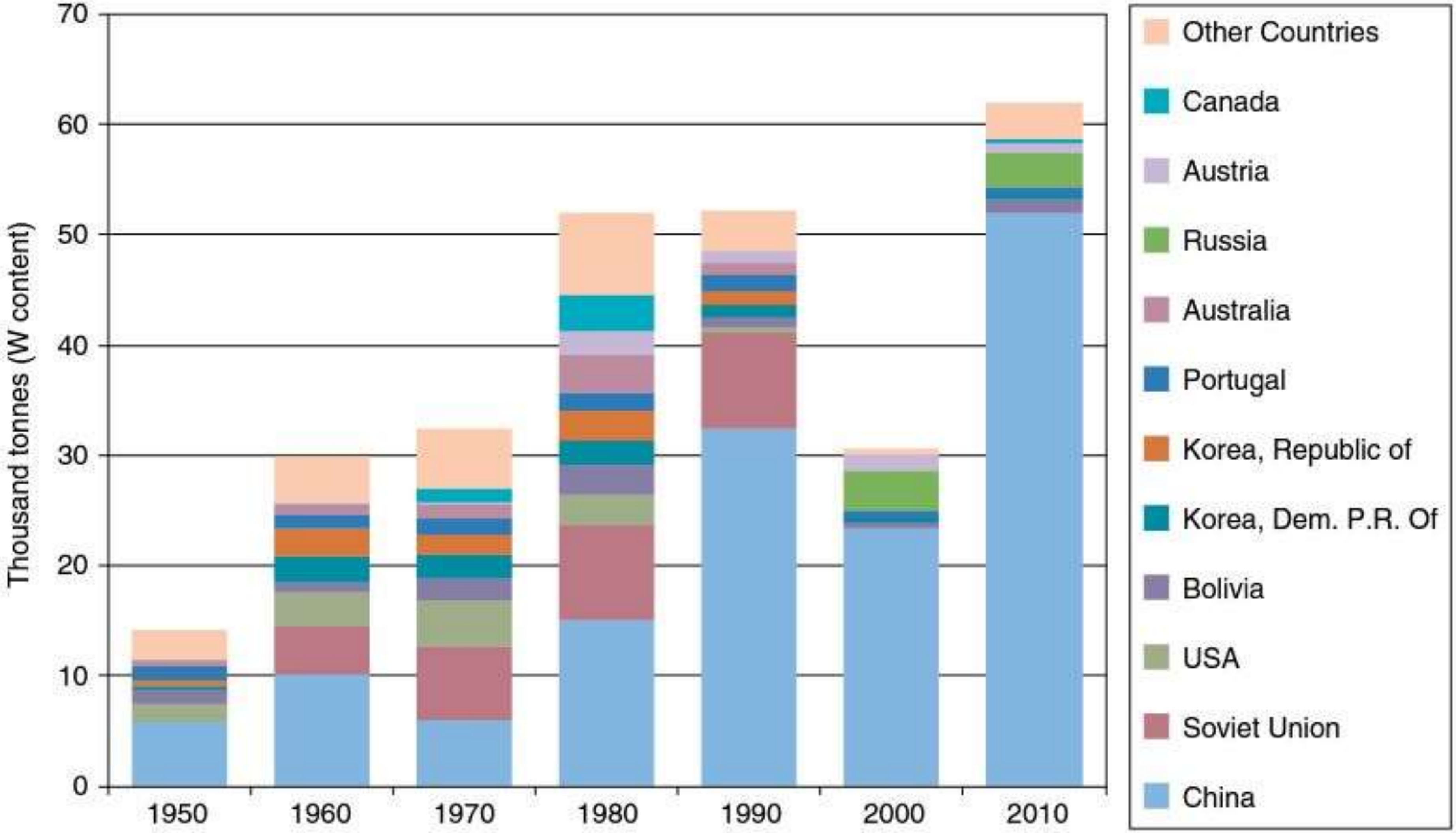


Figure 16.8 Evolution of tungsten production concentration, output by country for 1950, 1960, 1970, 1980, 1990, 2000 and 2010. (Data from British Geological Survey World Mineral Statistics database.)

W – major deposits under development

Table 16.4 Selected major tungsten deposits under development and those where production is expected in the near future.

Name	Country	Current Status (as at January 2013)	Possible Production	Resources (tonnes contained tungsten)
Hemerdon	United Kingdom	Feasibility study completed May 2011, mine construction expected 2013	2014	>460,000
Barruecopardo	Spain	Feasibility study completed Feb 2012, commissioning expected 2014	2014 or 2015	>50,000
Sangdong	South Korea	Feasibility study completed April 2012, commissioning expected 2014	2014 or 2015	>280,000
King Island	Australia	Feasibility study completed Feb 2012, all permits in place, raising funding	2015 ?	>190,000
Sisson Brook	Canada	Feasibility study completed 2013. Environmental impact assessment ongoing	2015 ?	>270,000
Cookes Creek	Australia	Feasibility study ongoing	Unknown	>40,000
Mactung	Canada	Feasibility study completed 2009, some environmental permitting in 2012	Unknown	>370,000
Northern Dancer	Canada	Preliminary economic assessment completed in 2011	Unknown	>390,000
O'Callaghans	Australia	Prefeasibility study ongoing	Unknown	>200,000

Note: Resources are from all categories and in some cases include reserves.

W – main tungsten exporting countries

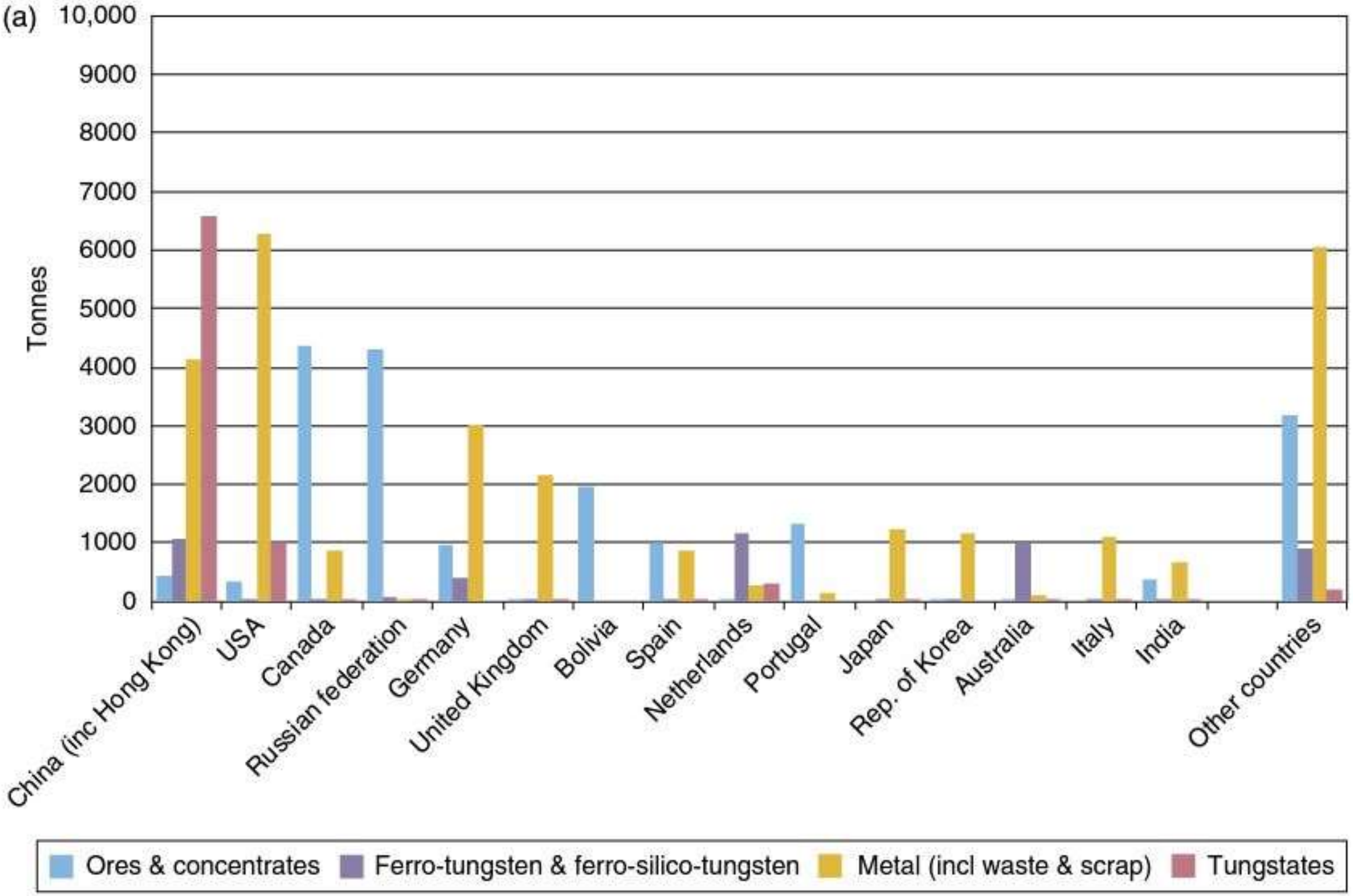


Figure 16.9a Main tungsten exporting countries, 2011. Note: 'tungstates' is predominantly APT. (Data from British Geological Survey World Mineral Statistics database and UN Comtrade, 2013.)

W – main tungsten importing countries

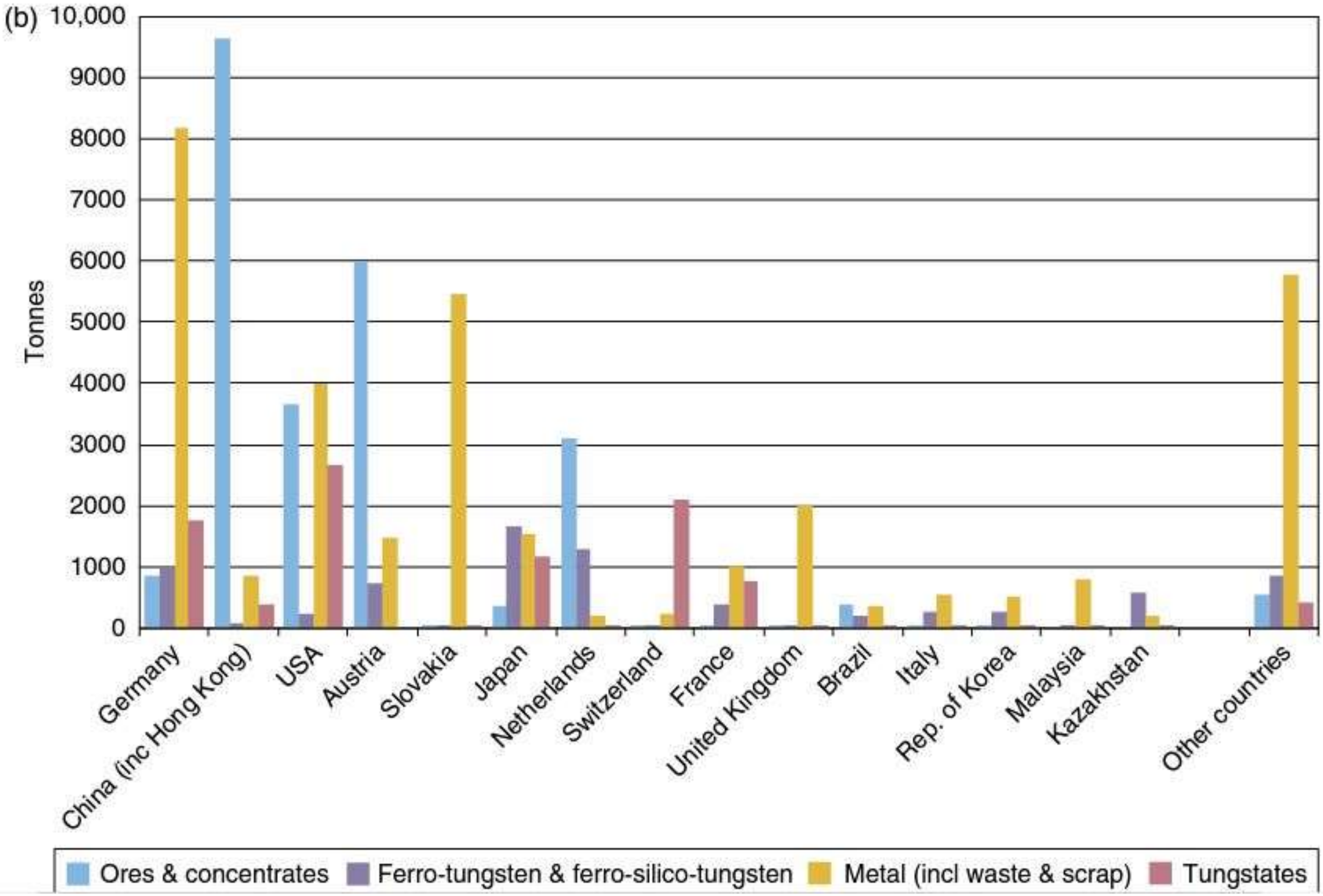
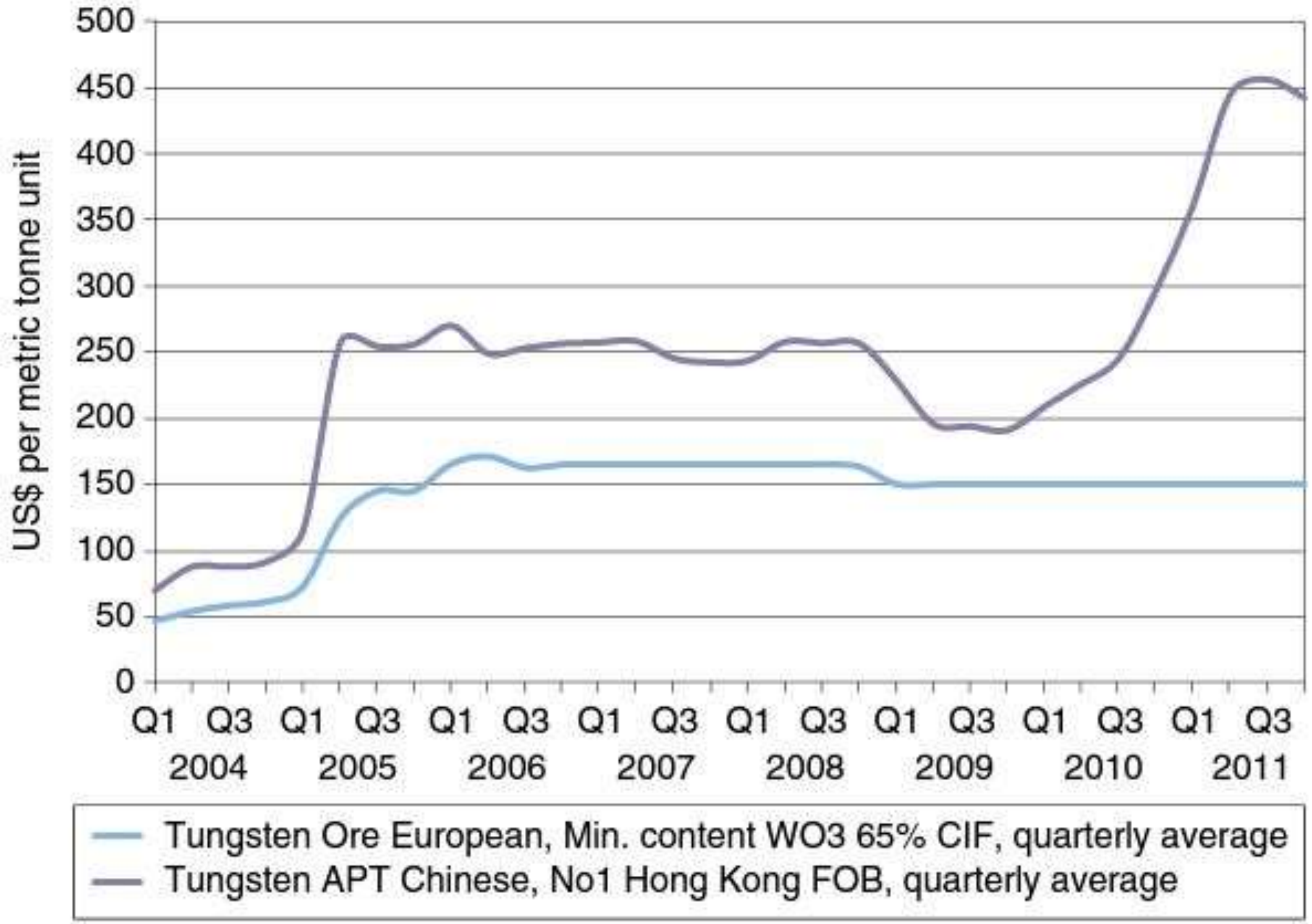


Figure 16.9b Main tungsten importing countries, 2011. Note: 'tungstates' is predominantly APT. (Data from British Geological Survey World Mineral Statistics database and UN Comtrade, 2013.)

W – tungsten ore and APT price trend



Tungsten ore and APT price trend 2004–2011 (Data from Metal Bulletin.)

W – environmental issues

- **W is much less toxic than other metals** (e.g. Pb and Hg, for which it is sometimes used as a substitute, e.g. in ammunition).

- Particles of **W metal** could **oxidize in air** and then dissolve into soil through the action of rainwater. Elevated levels of W have been found in soils, trees, plant tissues, aquatic systems, atmosphere, animals and humans.

- The dissolution of W powders appears to cause **soil acidification** with associated adverse consequences on the micro-organisms, invertebrates and plant communities.

- The **geochemistry of W is complicated** and its mobility, bioavailability and toxicity in the environment depends upon the exact form of **W compounds**, **pH**, **oxidation states** and the **nature of the exposure pathway**.

W – outlook

- The worldwide supply of W is dominated by **China** (> 70% of total world production).
- **Several new non-Chinese mines** are likely to start production in the near future.
- W use is largely influenced by conditions in the **global economy**.
- Future developments of **specialist steel alloys** and “**superalloys**” (high-T and wear resistance) are likely to require significant quantities of W → **aerospace, industrial turbines, fusion reactors**.

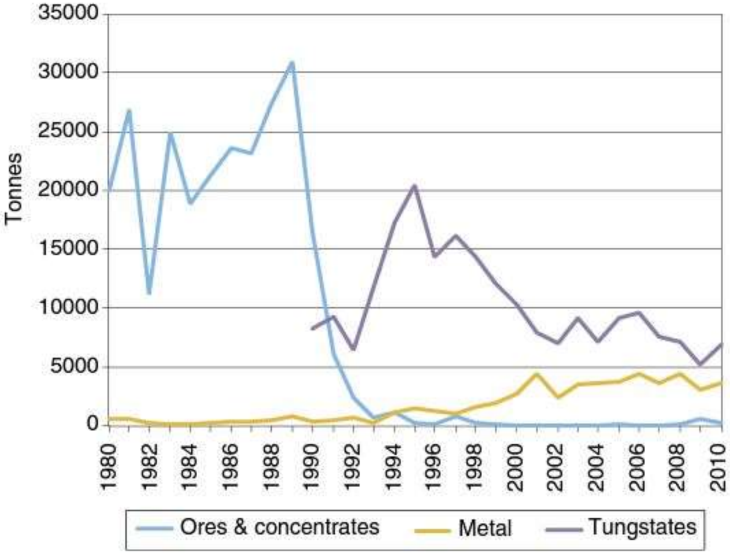


Figure 16.11 China exports of tungsten ores and concentrates compared to exports of tungstates (mainly APT) and tungsten metal, 1980–2010. (Data from British Geological Survey World Mineral Statistics database and UN Comtrade, 2013.)

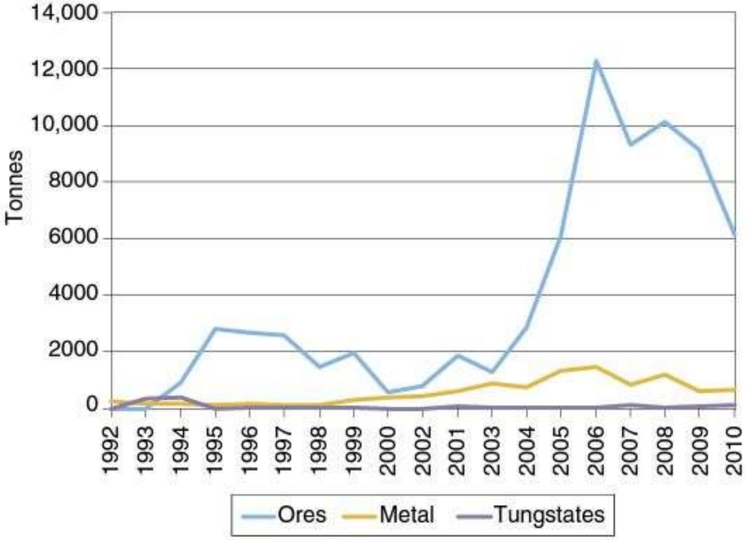


Figure 16.12 China imports of tungsten ores and concentrates, tungstates (mainly APT) and tungsten metal, 1992–2010. (Data from British Geological Survey World Mineral Statistics database and UN Comtrade, 2013.)