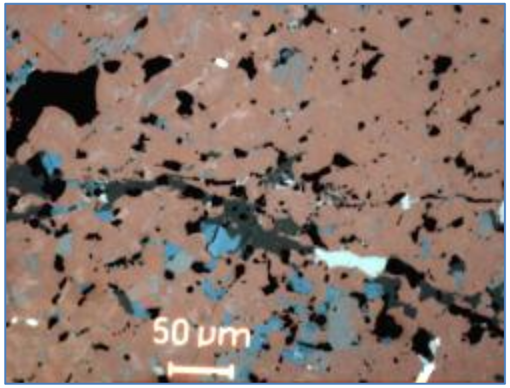
Current and future Germanium availability from primary sources

Dr. Frank Melcher & Dr. Peter Buchholz



Minor Metals Conference, Cologne, April 24, 2012

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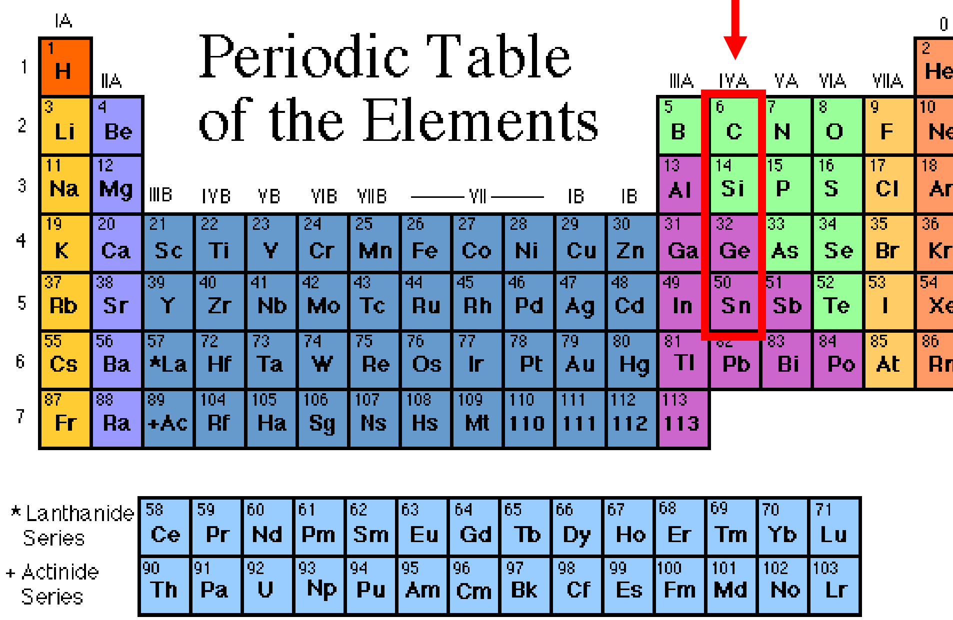
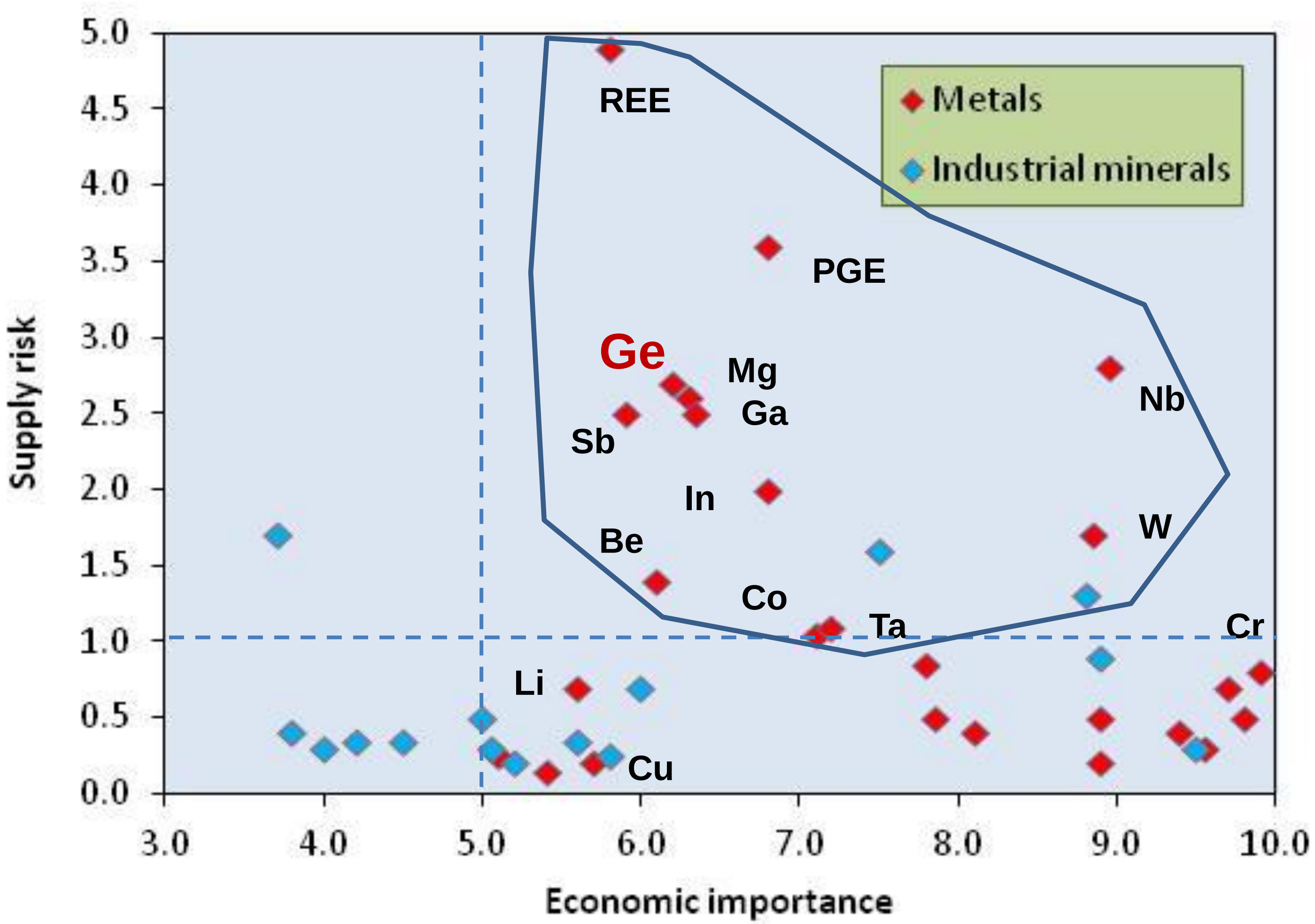
Germanium



The great Russian chemist Mendeleev (left), who had predicted the existence of the element Germanium (1871), und C. Winkler, who discovered it in the mineral Argyrodite (1886).

http://tw.strahlen.org/typloc/argyrodit.html

The EU-14 “Critical Minerals”



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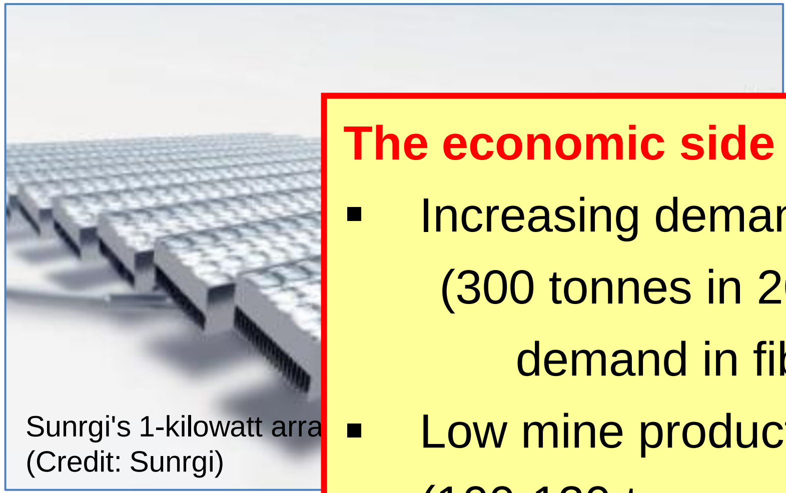
Germanium: properties

– Semiconductor
    - effective at high frequencies, low voltages
– Transparency to infrared light
– Glass-former (Ge-O tetrahedra networks)
– High refractive index
– Low chromatic dispersion
– Catalyzes polymerization in PET production

Germanium: A "High Technology Metal"



Sunrgi's 1-kilowatt arra
(Credit: Sunrgi)

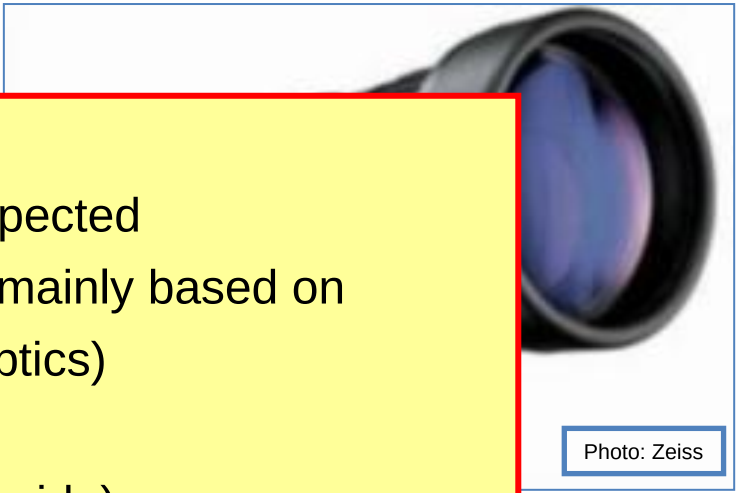
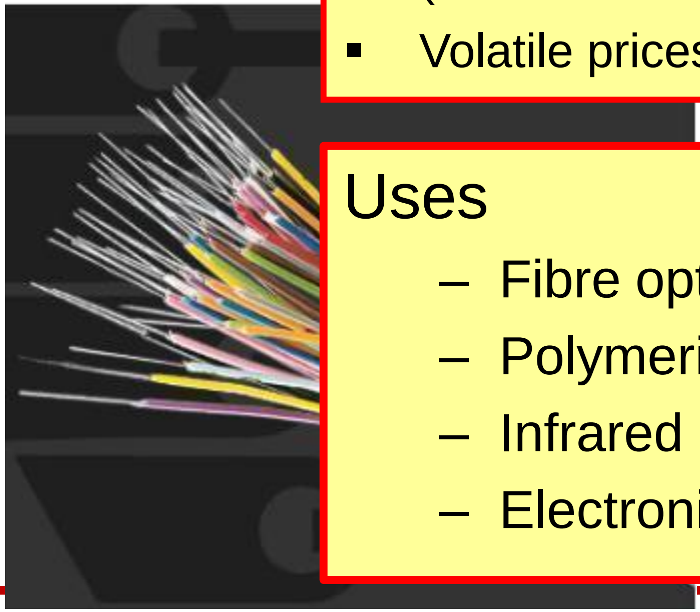
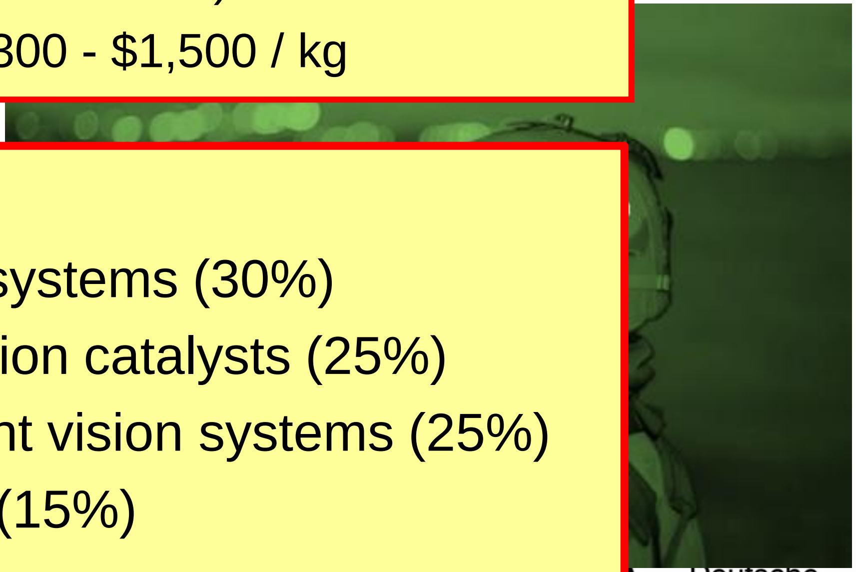


Photo: Zeiss





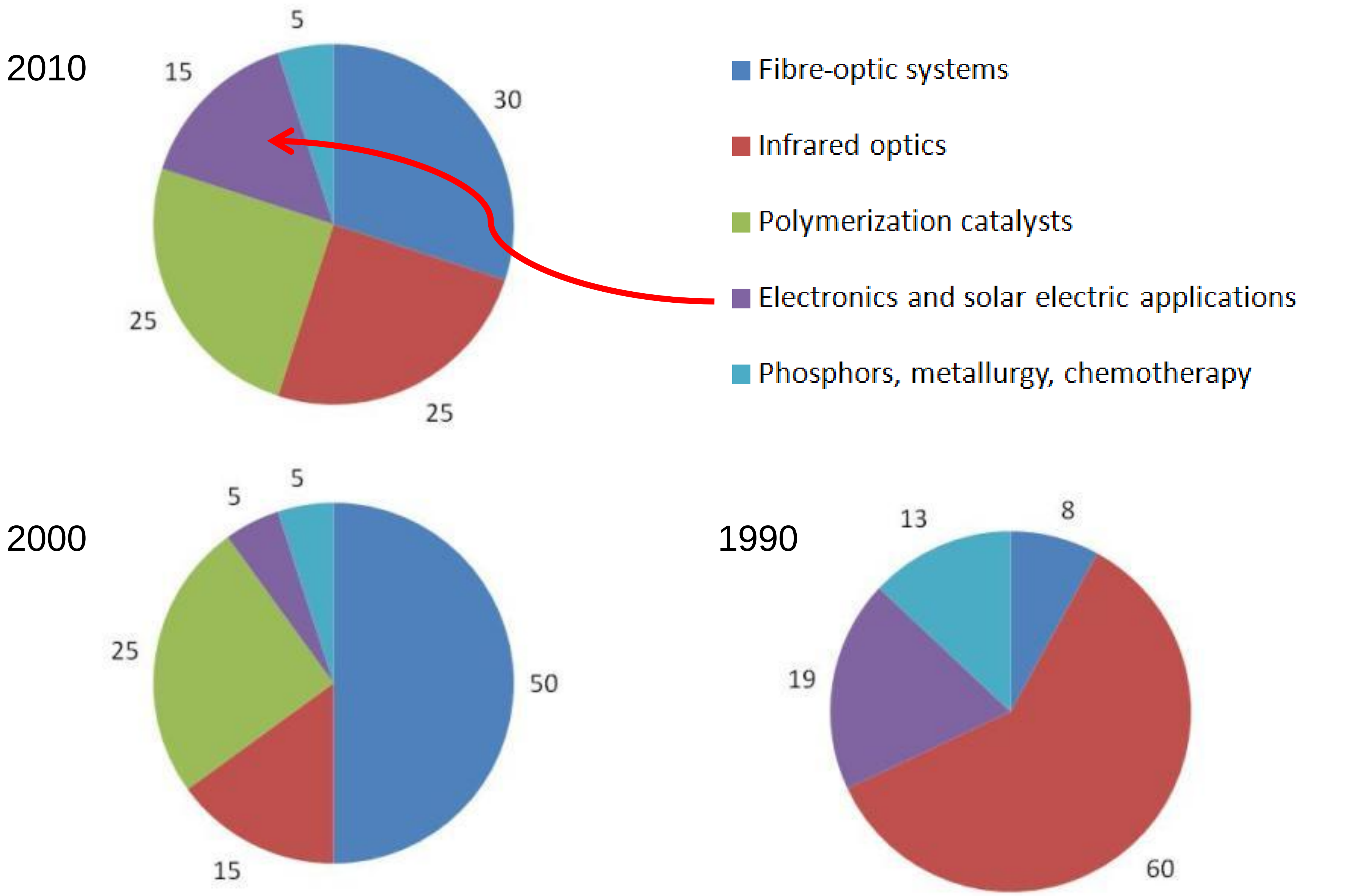
The economic side

- Increasing demand expected
  (300 tonnes in 2030, mainly based on
  demand in fibre optics)
- Low mine productions
  (100-120 tonnes worldwide)
- Volatile prices; $300 - $1,500 / kg

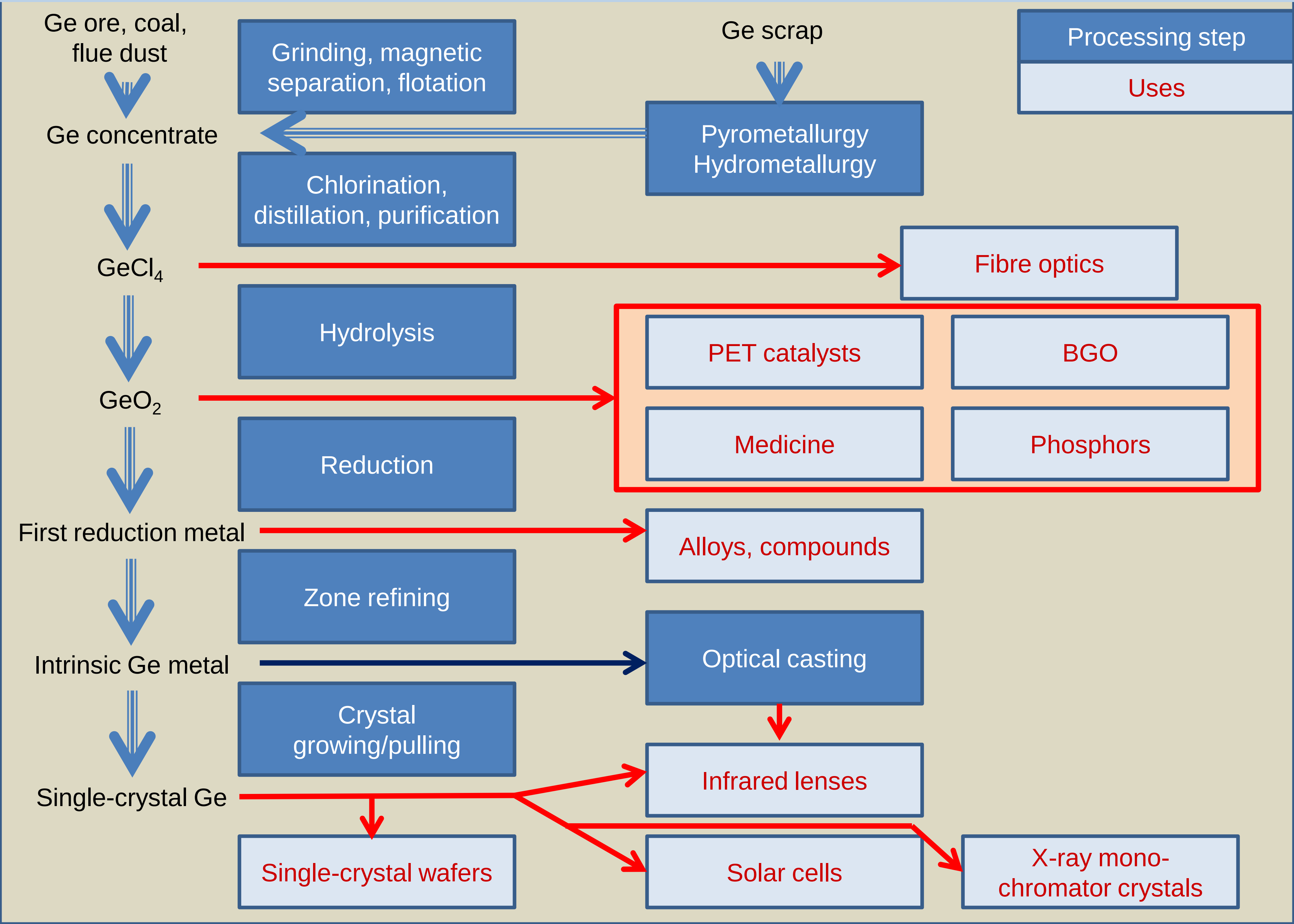
Uses

- – Fibre optic systems (30%)
- – Polymerization catalysts (25%)
- – Infrared night vision systems (25%)
- – Electronics (15%)

Germanium: end uses

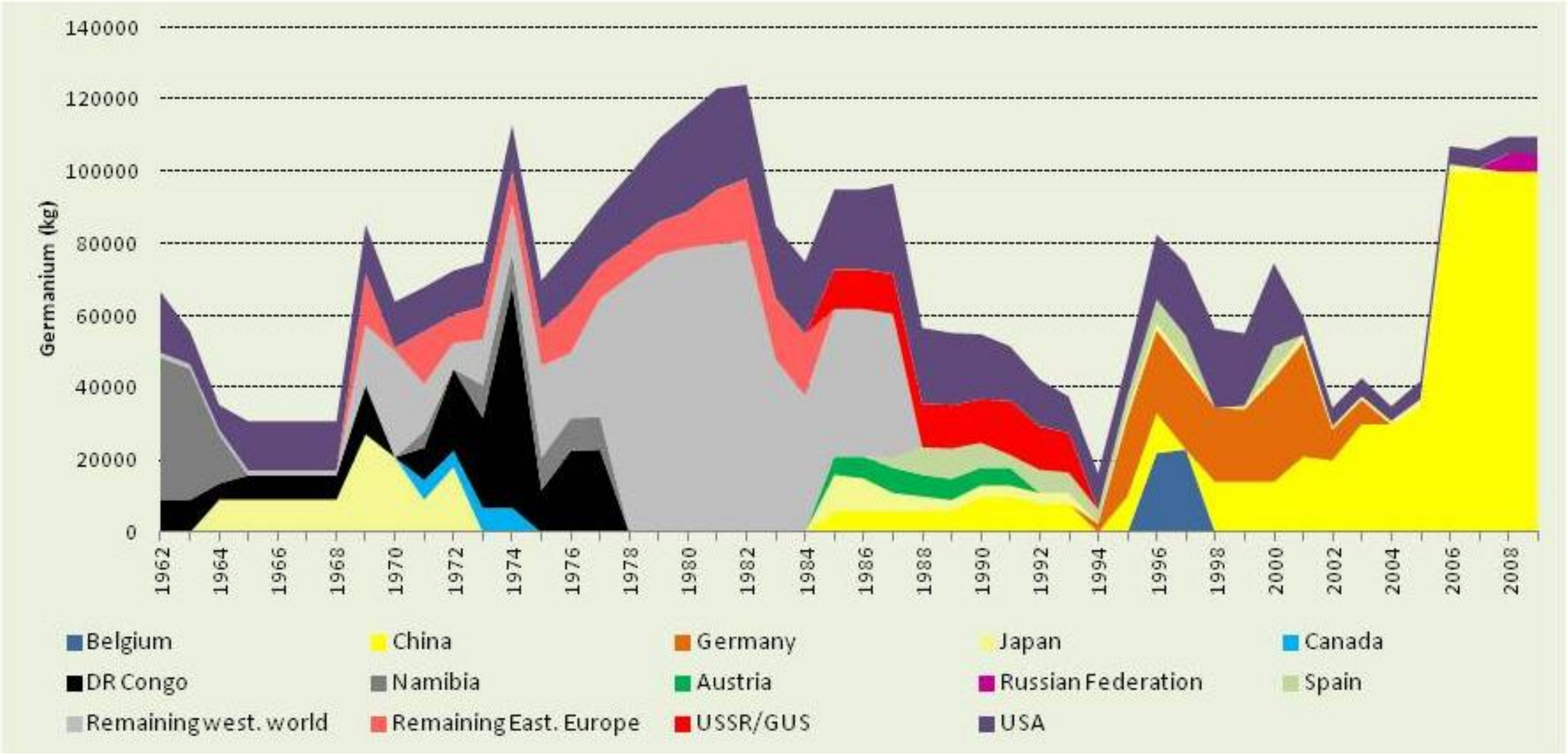


Germanium: Processing, beneficiation and uses



Market sector	End us	Prognosis 2030	Ge product
Fibre optics	30 %	+5-7% p.a.; >**200 t in 2030**	GeO_2 dopant in glass fibres
Infra-red optics	25 %	Increasing demand	Polycrystalline + single crystals; GeO_2 as component of glasses in camera lenses
Polymerization catalysts	25 %	Decreasing trend	GeO_2
Electronics	15 %	Increasing, rates uncertain	Si-Ge-based chips
Semiconductors		Increasing demand	Ge doped with Sb, As, P (n-type); Al, B, Ga (p-type)
Diodes		32% increase 2009-2014 (Ge Corp estimate)	Ge substrate for high brightness LEDs
Transistors		Increasing demand	Si-Ge bipolar transistors; Si-on-insulator technology
Solar cells		Increasing demand	Polished Ge wafers for multilayer solar cells (40% efficiency)
Radiation detectors	5 %	Unknown	Single crystals of ultra-pure Ge
Superconductors		Increasing	Melting Ge with metals (Nb_3Ge)
Medicine		Unknown	Ge-organic compounds

Historical Germanium Production



Data: USGS, BGR, BGS

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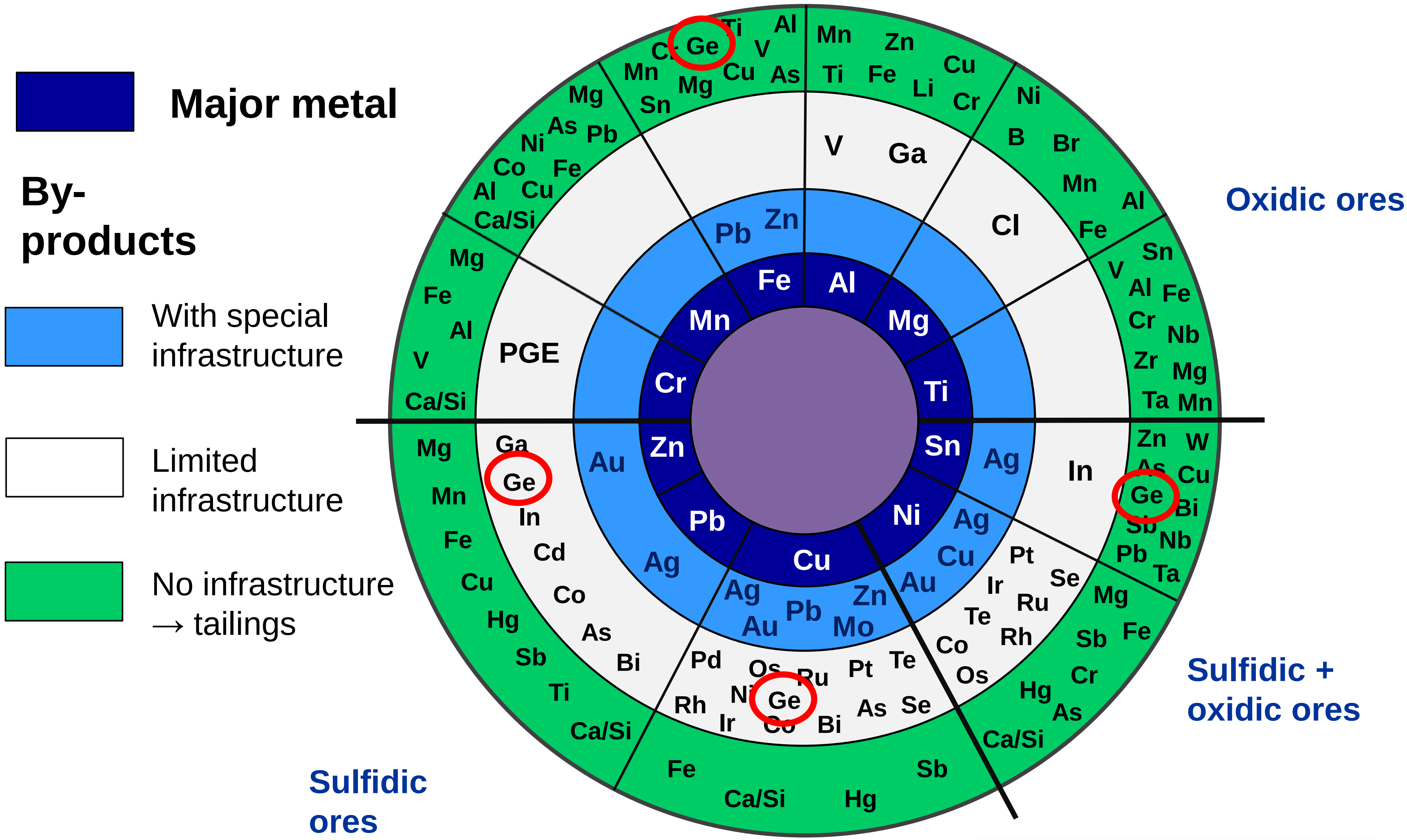
The "Metal Wheel"



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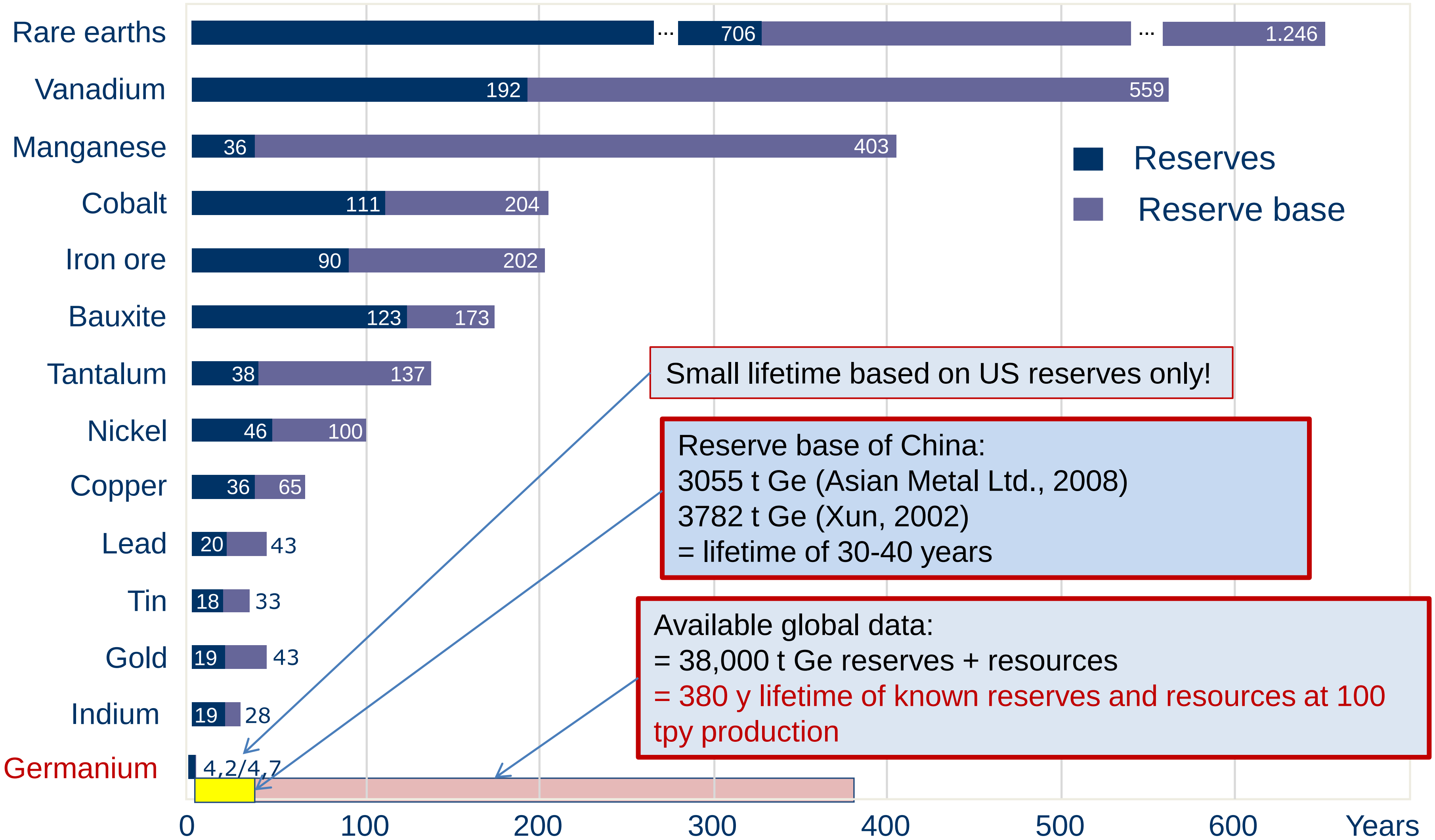
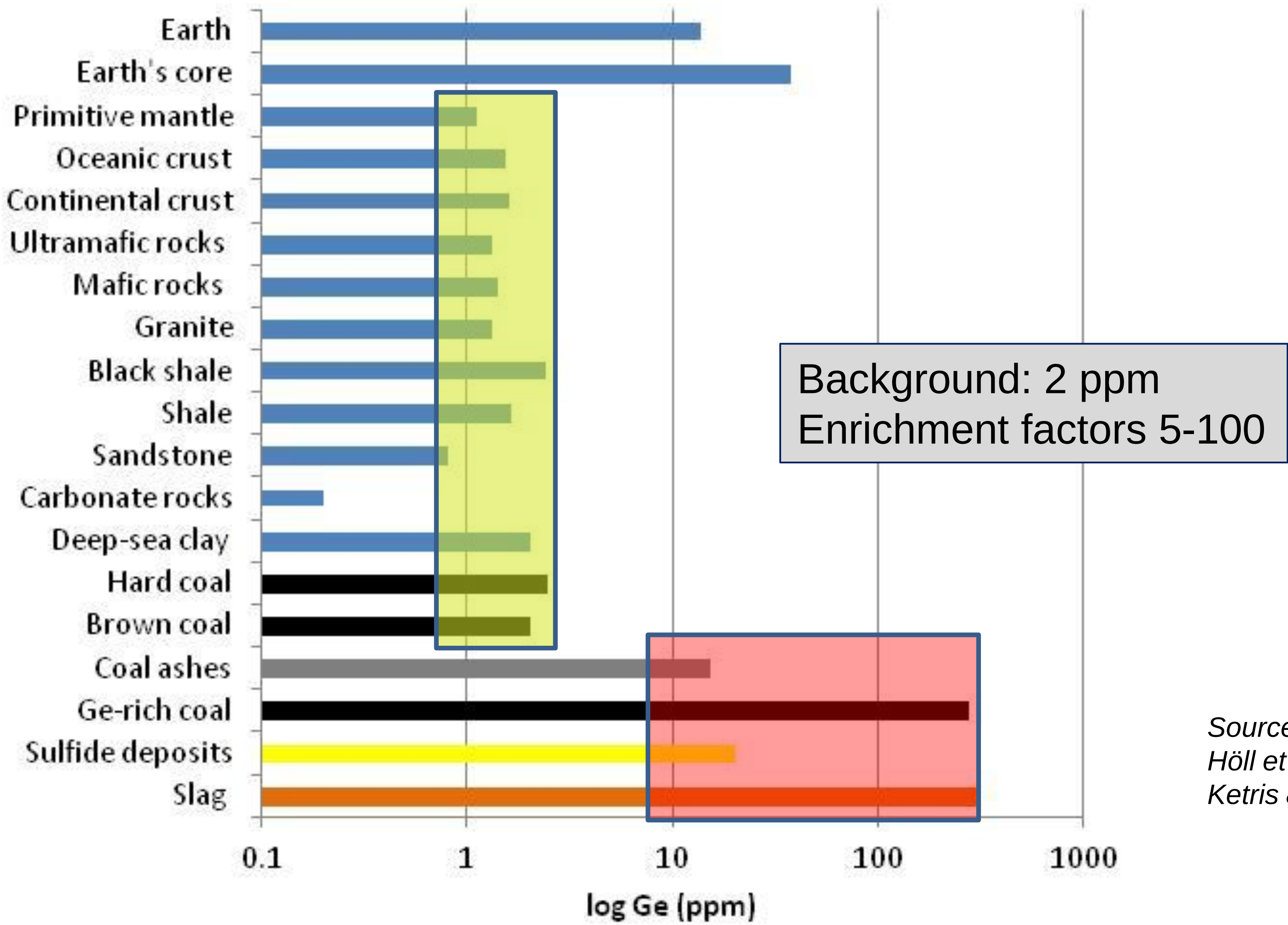
Lifetime of reserves: known reserves / annual production



Germanium: Abundance in rocks and ores



Sources:
Höll et al. 2007
Ketris & Yudovich 2009

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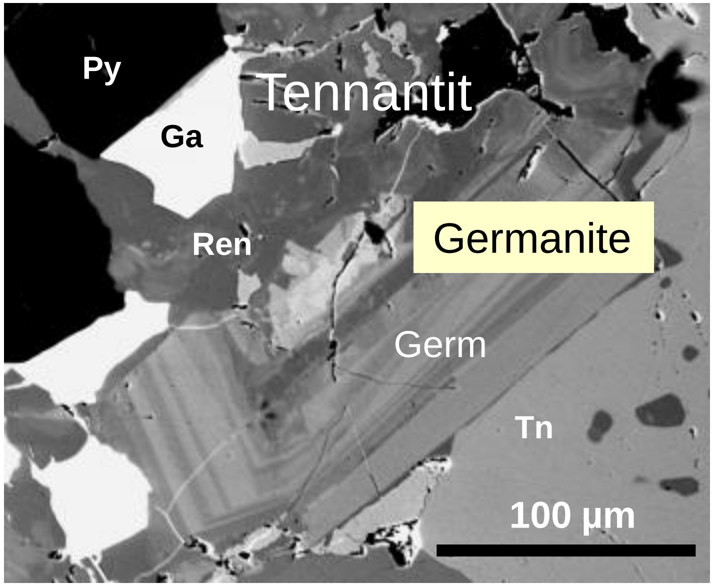
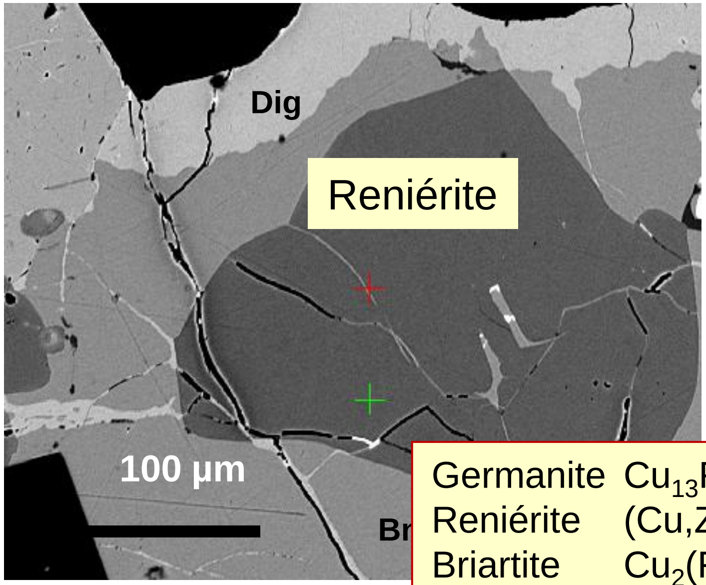
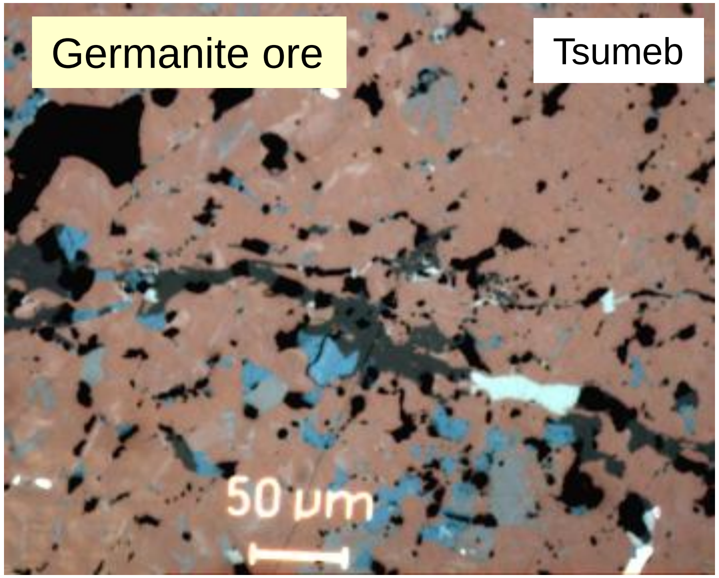
Germanium mineralogy

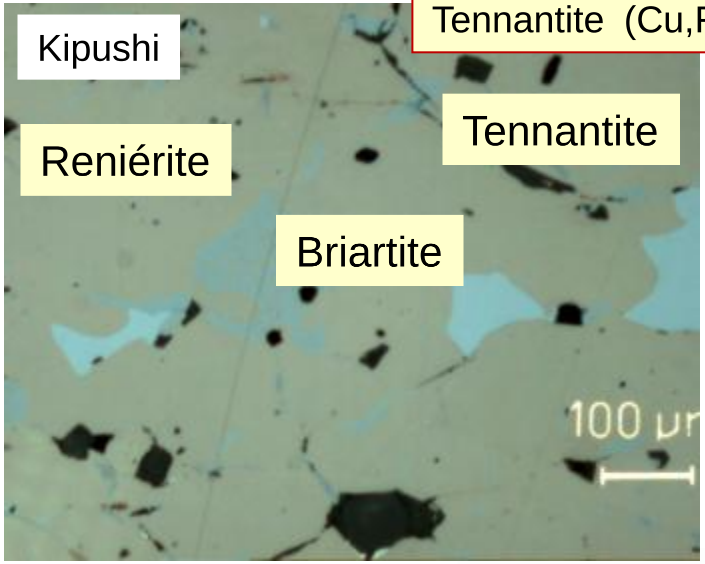
- **<u>ca. 30 Ge minerals occur in nature but are rare</u>**
- **Recovery of Ge from:**
  - **Ge-sulfides (germanite, reniérite, …)**
  - **Ge substituted in Zn and Cu-sulfides**
    - **up to 0.3 % Ge in sphalerite**
  - **Ge fixed in Fe oxyhydroxides**
  - **Ge adsorbed in coal**

Ge sulfides: major carriers of Ge at Tsumeb and Kipushi





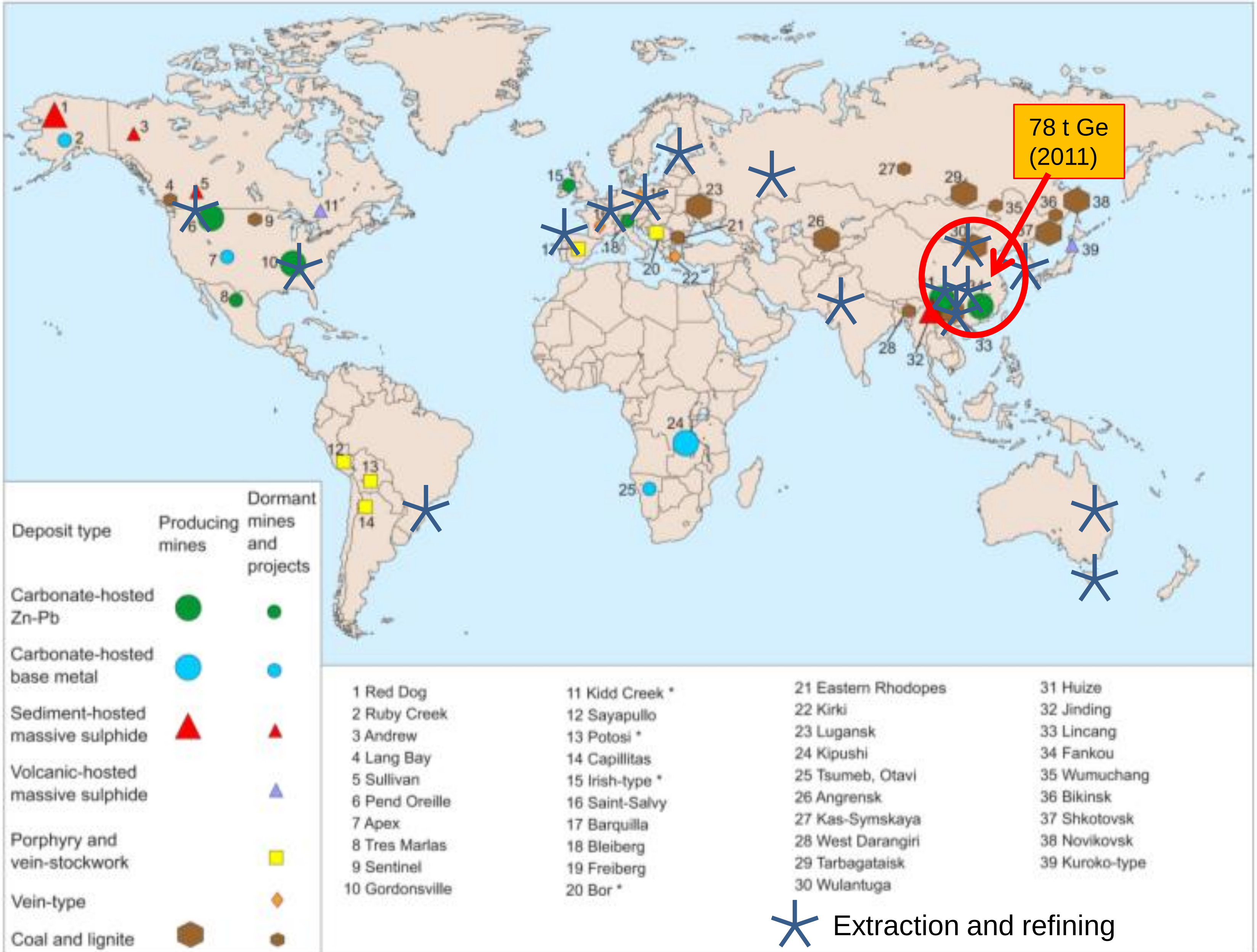




Germanite	$Cu_{13}Fe_2Ge_2S_{16}$
Reniérite	$(Cu,Zn)_{11}(Ge,As)_2Fe_2S_{16}$
Briartite	$Cu_2(Fe,Zn)GeS_4$
Tennantite	$(Cu,Fe,Zn)_{12}As_4S_{13}$

Germanium: Deposit types

Class	Type	Past production	Potential	Typical ore grade Ge (ppm)
1	Volcanic-hosted Cu-Zn	low	medium	<<100 (-300)
2.1	Porphyry Cu-Mo-Au	low	low	10 - 100
2.2	Porphyry Sn-Ag	low	medium	10 - 100
3	Vein-type (Ag-Pb-Zn)	high (pre-1993)	low	100 - 1000
4	Sediment-hosted Zn-Pb-Cu	high	high	10 - 100
5.1	Carbonate-hosted Zn-Pb	high	high	10 - 1000
5.2	Kipushi-type polymetallic	high	medium	10 - 1000
5.3	Oxidation of 5.2 (Apex-type)	medium	low	100 - 1000
5.4	Non-sulfide Zn-Pb	low	low	10 - 100
6	Sediment-hosted stratiform Cu	low	medium	1 - 20
7	Iron oxide ores	none	low	10 - 50
8	Coal and lignite	medium/high	high	100 - 1000



From: Melcher & Buchholz, Critical Metals Handbook, Wiley 2012 (in press)

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Active and potential Ge producers from sulfide ore and slag

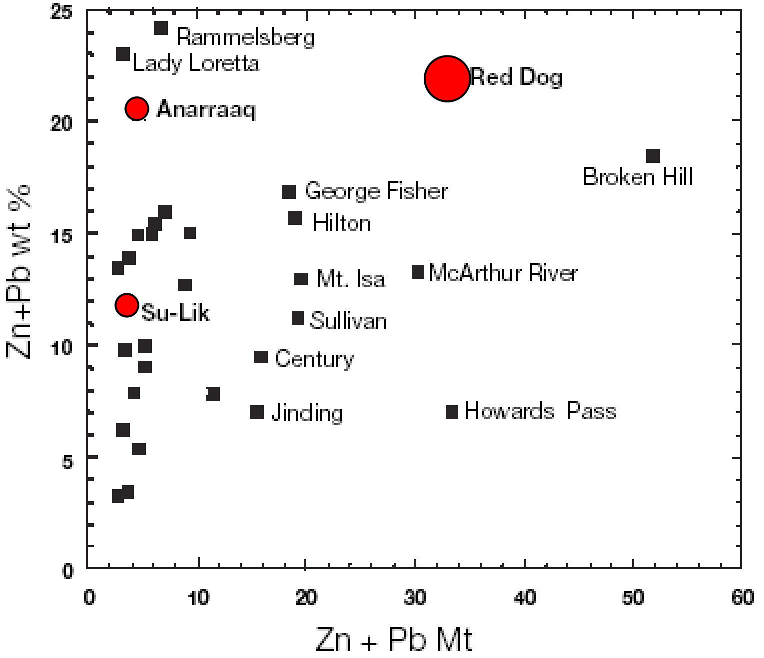
Deposit	Country	Type	Ge resources	Ge grade (ppm)	Status
Huize	China	Sulfide	600	40	production
Jinding	China	Sulfide	3000	10-100	production
Fankou	China	Sulfide	600	100	production
Red Dog	USA	Sulfide	1200	15	production
Lubumbashi	DR Congo	Slag	2250	100-250	production
Kipushi	DR Congo	Sulfide	1500	68	dormant
Andrew	Canada	Sulfide	88	18	exploration
Tres Marias	Mexico	Sulfide	150	150	exploration
Pend Oreille	USA	Sulfide	300	10-100	dormant
Gordonsville	USA	Sulfide	800	20	dormant
Kolwezi	DR Congo	Slag	?	500 ?	exploration
Tsumeb	Namibia	Slag	530	260	exploration
Total			11,000	Metric tons	

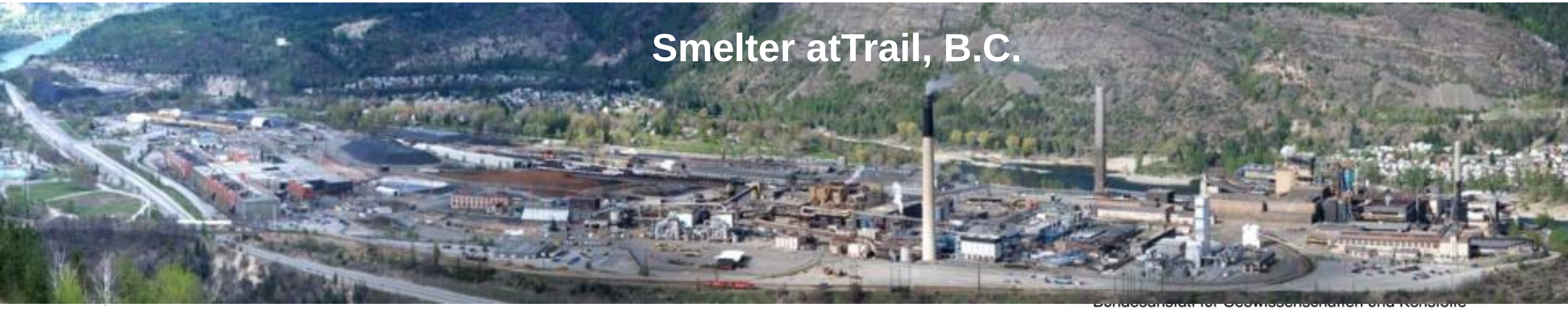
Red Dog Mine, northwest Alaska

Teck Resources

- World s largest zinc mine (SEDEX deposit)
- **Production** *(InfoMine, 2009)*:

  583.000 t Zn and 132.000 t Pb
- ca. 60 t Ge contained
- 15 t Ge produced at Trail, capacity 28 tpa
- **Reserves**: 51.6 Mt at 16.7 % Zn, 4.4 % Pb
- **800-1600 t Ge resources (estimate)**
- 106 ppm Ge (<0.5 – 823 ppm; Slack et al., 2004) in sphalerite





Tres Marias Project

War Eagle Mining Co.

Zn sulfide + "oxide" deposit

carbonate-hosted

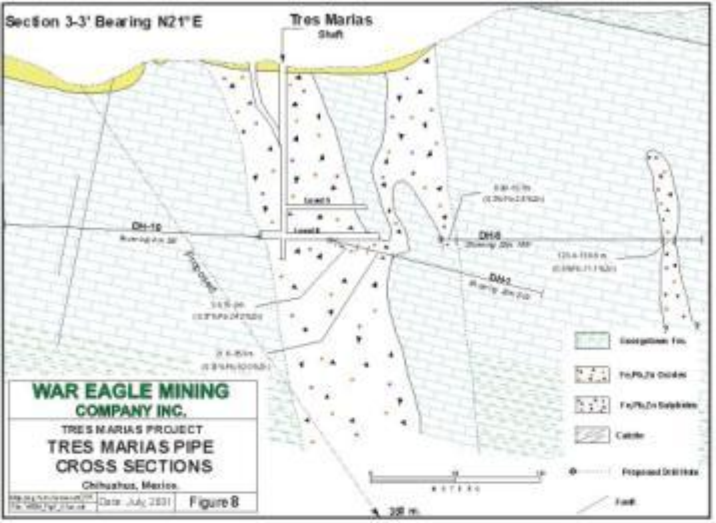
339 ppm Germanium

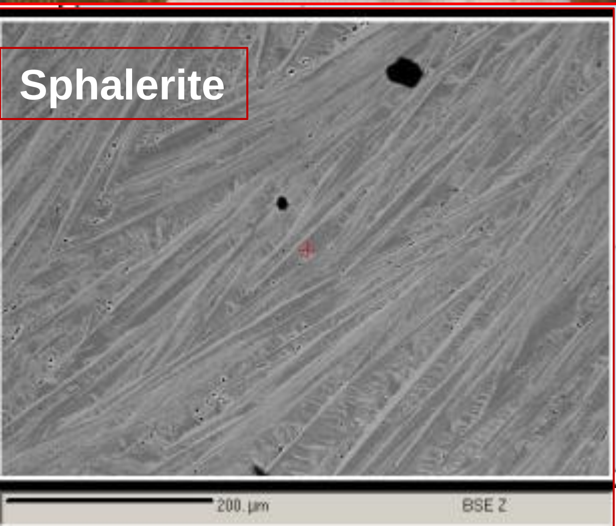
45 ppm Gallium

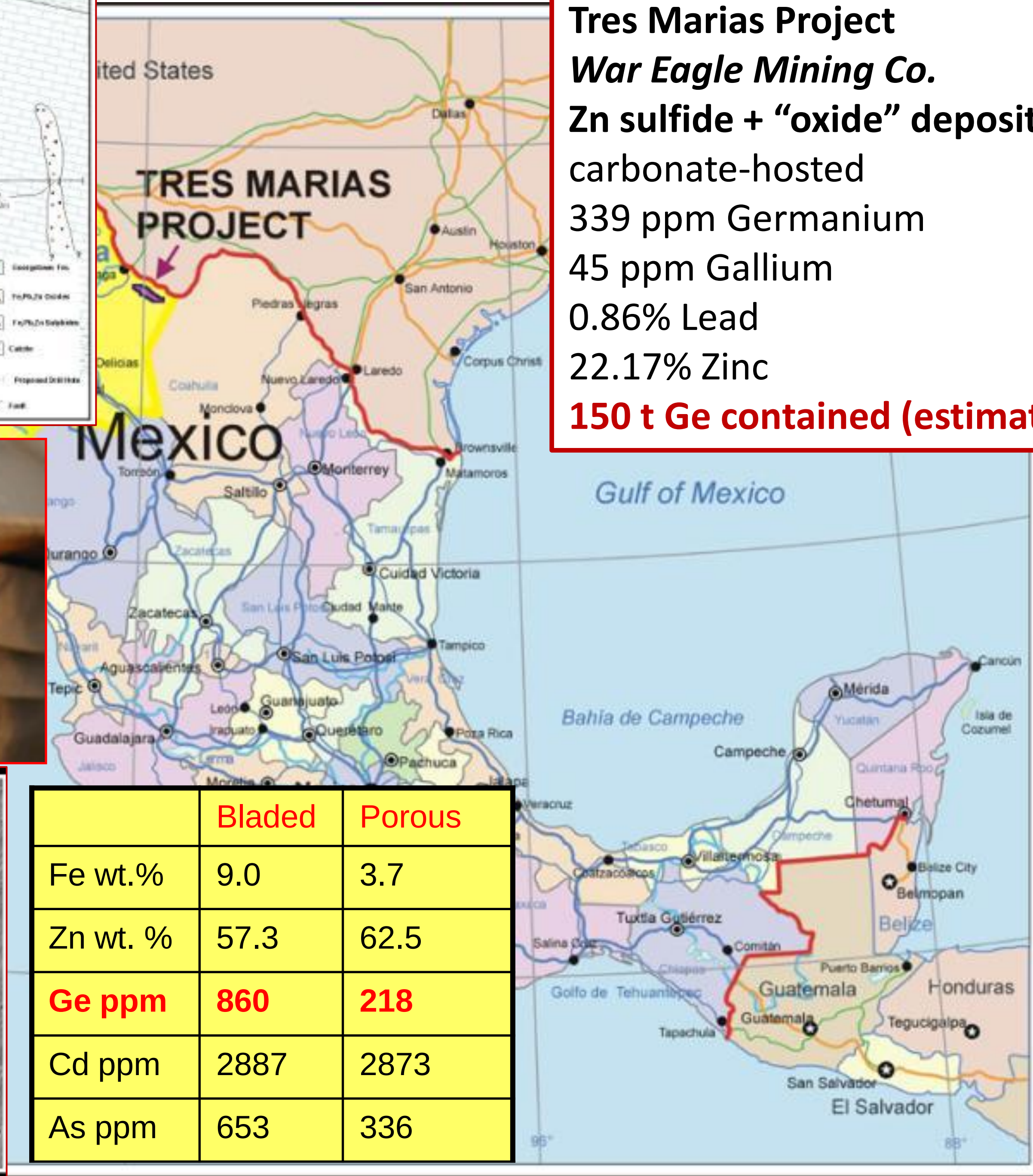
0.86% Lead

22.17% Zinc

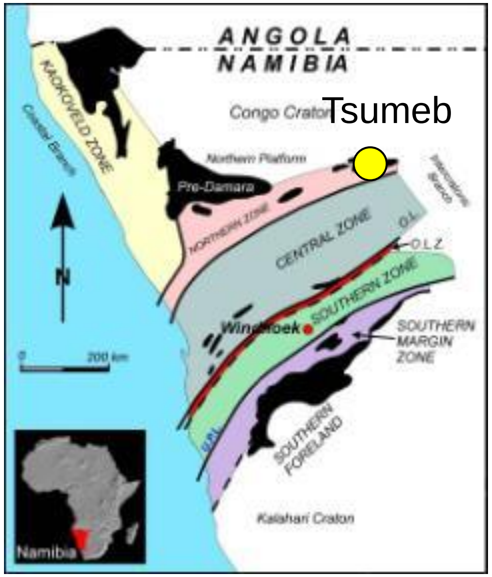
150 t Ge contained (estimate)







	Bladed	Porous
Fe wt.%	9.0	3.7
Zn wt. %	57.3	62.5
Ge ppm	**860**	**218**
Cd ppm	2887	2873
As ppm	653	336



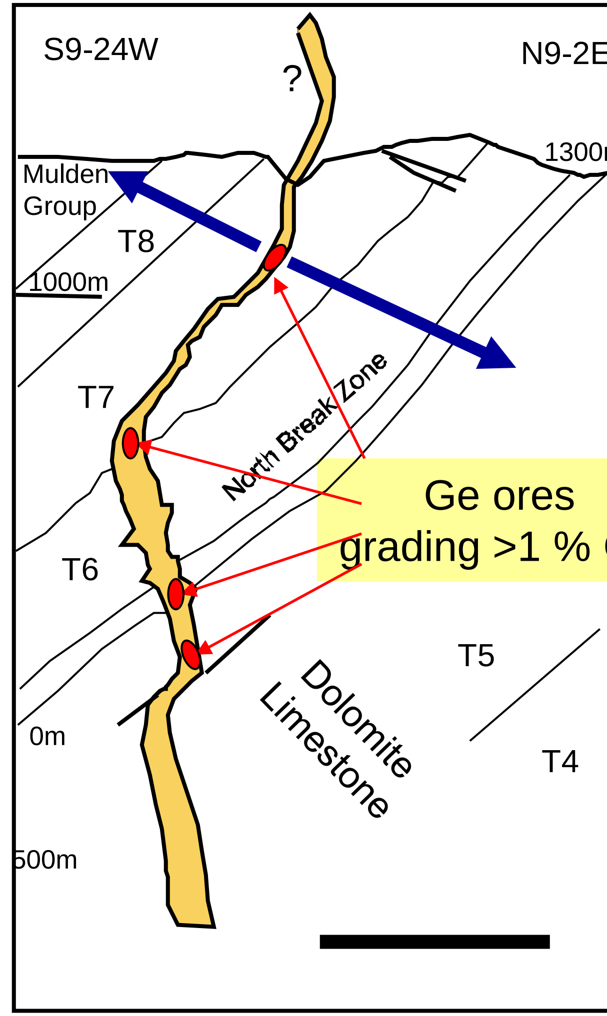
Tsumeb-/Kipushi-type

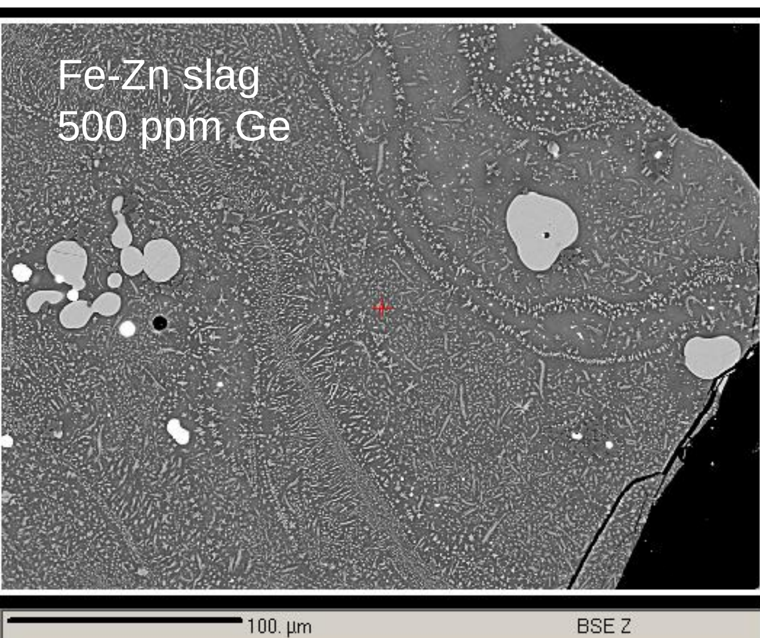
Major Ge source until 1990

Carbonate-hosted polymetallic sulfide ores (Cu-Zn-Pb-Ag-Ge-Ga-Cd-Mo-W)

Potential Tsumeb / Namibia
> 1000 t Ge
<100 t extracted

Tsumeb pipe





The "Big Hill" of Lubumbashi, DRC: a possible source of germanium

STL plant (since 2000)
55 % OM Group (U.S. - Finland)
25 % Groupe Forrest (Congo D.R.)
20 % Gécamines (Congo D.R.)
Production: 4,000 t Co, 2,500 t Cu, 15,000 t Zn
a few tons of Ge p.a. (?)

15 Mt slags from 80 years of production
(Kipushi Ge-rich Zn-Cu ore plus stratiform Cu-Co ores)
Core: 0.4 % Co, 12.5 % Zn, 1.3 % Cu, **250 ppm Ge**
Margin: 1.2 % Co, 12 % Zn, 2 % Cu, **100 ppm Ge**

Potential > 2,250 t Ge
= 20 years of world supply !

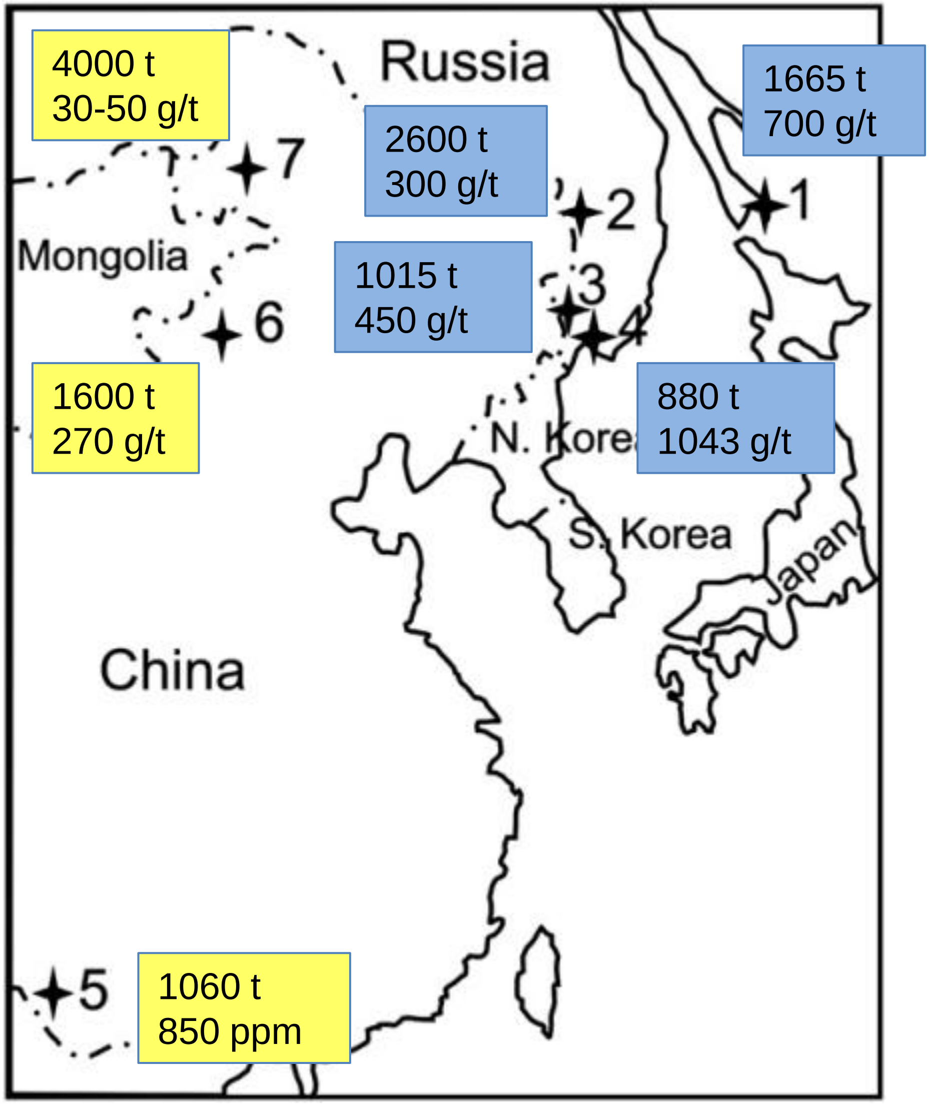
Germanium in coal

- 30 % of current primary Ge production is from coal
- Most Ge-rich coal (mainly lignite) is restricted to China and Russia
- Average of up to 1000 ppm Ge in some lignites; up to 1% Ge in ash
- Global resources are huge
  - 24,600 tons Ge estimated by Melcher & Buchholz (2012)
- No Ge production from coal in western countries
- Poor Ge recovery (ca. 60%), using microorganisms 85% feasible
- Recent BGR investigation:
  - German import coal contains low Ge (<4 ppm)
  - German lignite contains low Ge (<1 ppm)

Active and potential Ge producers from coal and coal ashes

Deposit	Country	Type	Ge resources	Ge grade (ppm)	Status
Lincang	China	Lignite	1060	850	production
Wulantuga	China	Lignite	1600	270	production
Novikovsk	Russia	Lignite	1665	700	production
Luchgorsky	Russia	Lignite	2600	300	production
Lugansk	Ukraine	Anthracite			production
Angrensk	Uzbekistan	Hard coal	180	30	production
Tigninskiy	Russia	Lignite	340	53	production?
Pavlovsk	Russia	Lignite	1015	450	production?
Shkotovsk	Russia	Lignite	880	1043	closed
Kas-Symskaya	Russia	Lignite	11,000	205	exploration
Wumuchang	China	Lignite	4,000	30-50	exploration
Church	USA	Lignite	165	40-70	exploration
Total ca.			25,000	Metric tons	

The Eastern Asian Germanium-rich Coal Province

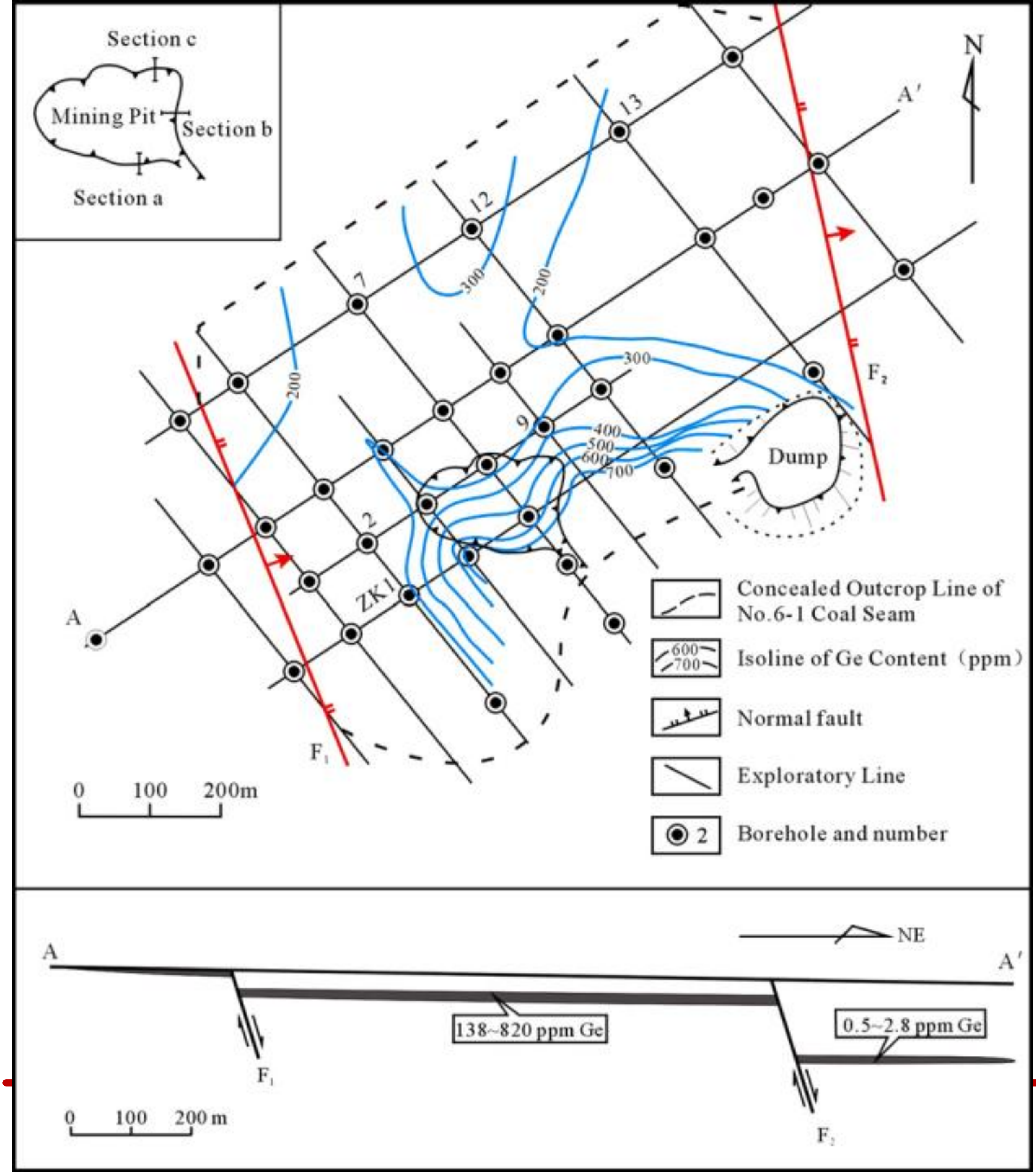


Position of the largest Ge–coal deposits of the World.

1 — Novikovsk
2 — Bikinsk
3 — Pavlovsk
4 — Shkotovsk
5 — Lincang
6 — Wulantuga
7 — Wumuchang

(Seredin & Finkelman, 2008, Int J Coal Geol)

13,000 t Ge reserves in 7 coal fields



Wulantuga Germanium Deposit , Inner Mongolia

Resources 1600 t Ge
Grade 270 ppm Ge

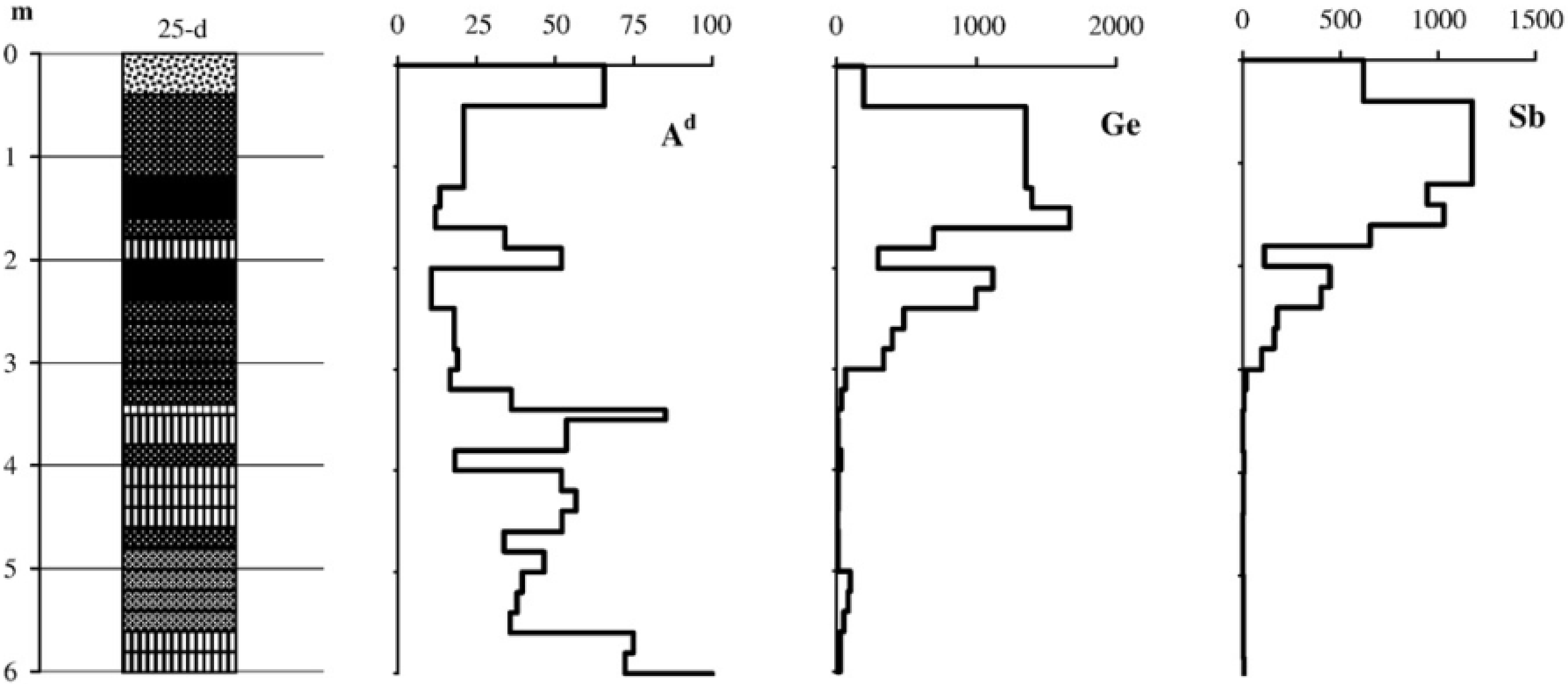
Isopach map of Ge content in lignite

Qi et al. 2007 Int J Coal Geol

Pavlovsk lignite deposit, Russia

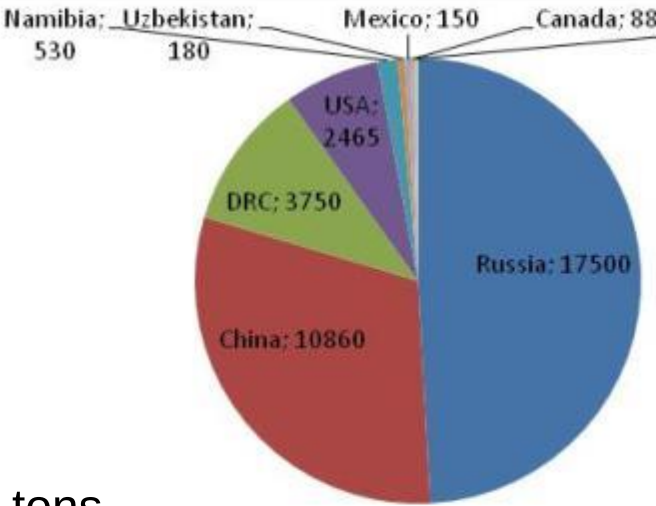
1015 t Ge resources, 450 ppm Ge grade

Distribution of ash content, Ge and Sb



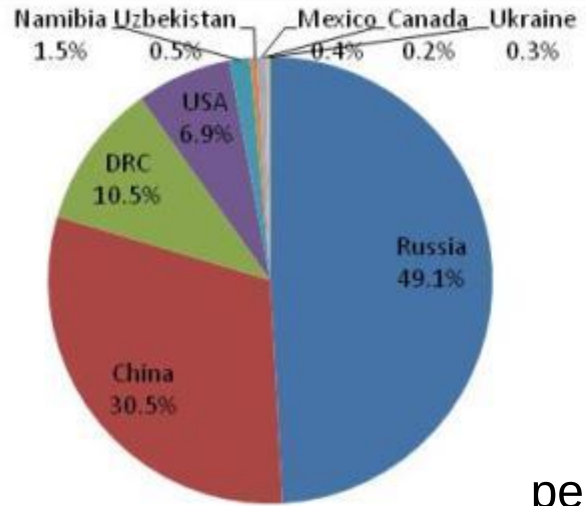
Seredin & Finkelman, 2008, Int J Coal Geol

Germanium: resource estimates

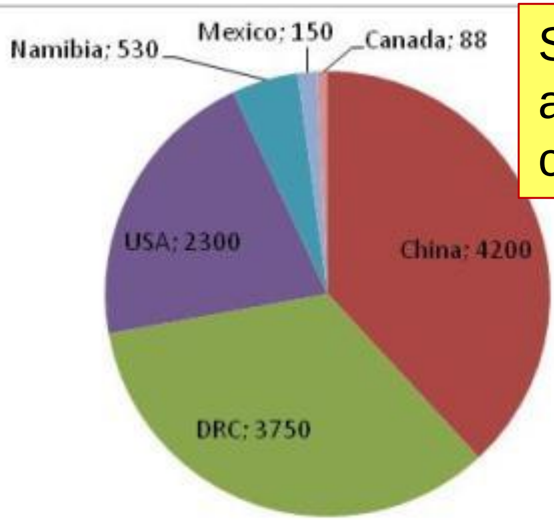


tons

All resources
ca. 35,600 t

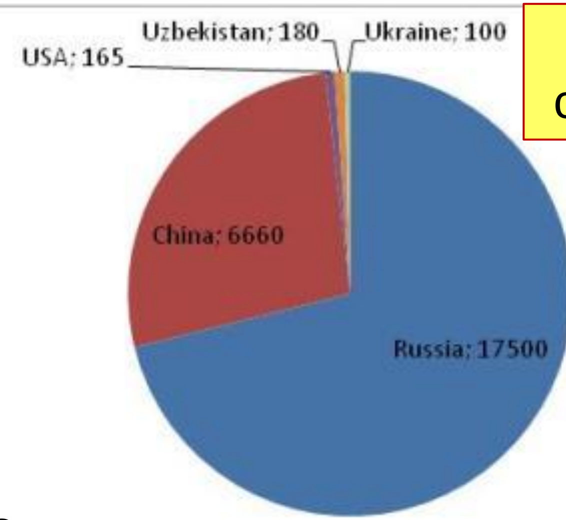


percent



Sulfide ores
and slags
ca. 11,000 t

tons



Coal
ca. 24,600 t

tons

Production capacity of active and potential Ge producers

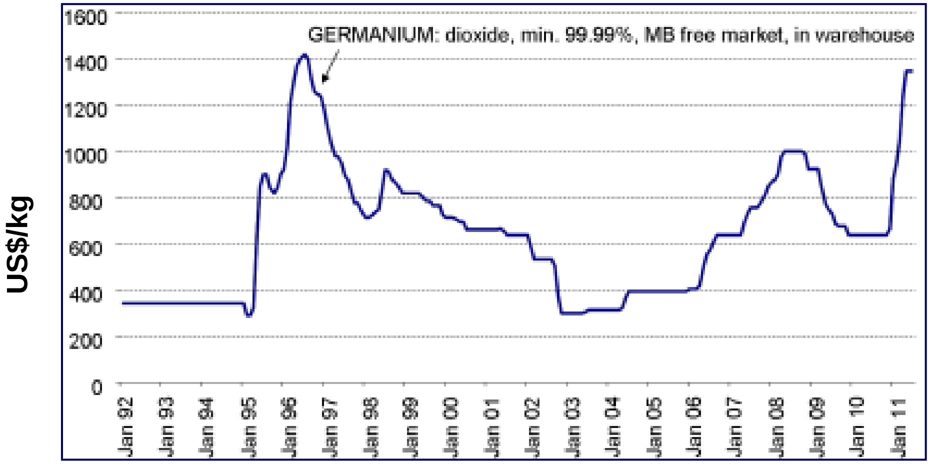
Deposit	Country	Type	Ge resources (metric tons)	Ge production capacity (tpa) (installed/max)	Current Status
Huize	China	Sulfide	600	10 / 30	production
Jinding	China	Sulfide	3000	10 / 10	production
Fankou	China	Sulfide	600	15 / 15	production
Red Dog	USA	Sulfide	1200	28 / 60	production
Tres Marias	Mexico	Sulfide	150	0 / 10	exploration
Pend Oreille	USA	Sulfide	300	0 / 50	dormant
Gordonsville	USA	Sulfide	800	0 / 35	dormant
Lubumbashi	DR Congo	Slag	2250	2 / 20	production
Tsumeb	Namibia	Slag	530	0 / 10	exploration
Lincang	China	Coal	1060	25 / 25	production
Wulantuga	China	Coal	1600	5 / 20	production
Novikovsk etc.	East Russia	Coal	6200	5 / 20	production
Total			>18,000	100 / 305	
Proportion of coal to sulfide + slag				35 / 21 %	

Germanium: recycling

– Little recycling from postconsumer scrap
– 25-35% of total Ge used from recycled scrap

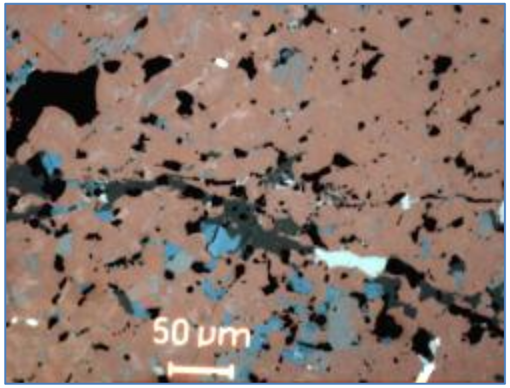
- Infrared optics: 30% production from recycled material
- Fibre optics: 60% recycled material; recovery from fibres 80%; 0.3-1 g GeO_2 per km cable
- Electronics, solar: 50% waste accumulation, recycled
- Polymerization catalysts: 10-70 ppm in PET bottles, no recycling of Ge possible

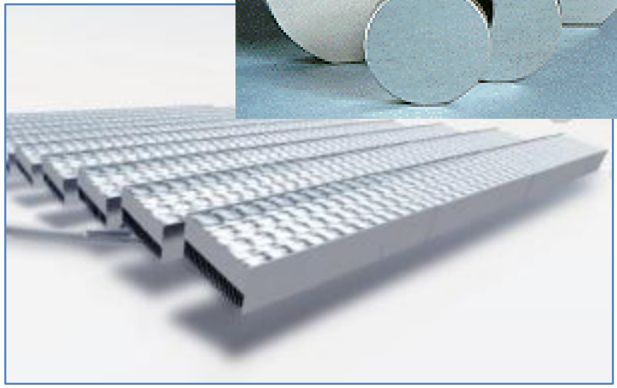
Conclusion: Germanium supply



Fiber optic cables, IR optical technologies	
Production 2006 - 2010: 100 - 120 t	Demand 2030 : ca. 300 t (72 + **220** t)
Development of production until 2030	
Active and planned mine capacities	ca. 300 t / year
Other sources / technologies: Recycling potential Improved recovery technologies	ca. 40 - 80 t / year
Situation alarming **High country concentration, country risk (China)**	
Production: By-product from Zn-Cu-ores (USA, China) and coal (China, Russia)	

Thank you





References: *Melcher & Buchholz, Critical Metals Handbook, Wiley 2012 (in press)*

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