Current and future Germanium availability from primary sources

Dr. Frank Melcher & Dr. Peter Buchholz
Germanium

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

http://tw.strahlen.org/typloc/argyrodit.html
The EU-14 “Critical Minerals”
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”

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

- 2010
  - Fibre-optic systems: 30%
  - Infrared optics: 25%
  - Polymerization catalysts: 25%
  - Electronics and solar electric applications: 15%
  - Phosphors, metallurgy, chemotherapy: 5%

- 2000
  - Fibre-optic systems: 50%
  - Infrared optics: 25%
  - Polymerization catalysts: 25%
  - Electronics and solar electric applications: 5%
  - Phosphors, metallurgy, chemotherapy: 5%

- 1990
  - Fibre-optic systems: 13%
  - Infrared optics: 8%
  - Polymerization catalysts: 19%
  - Electronics and solar electric applications: 60%
Germanium: Processing, beneficiation and uses

Ge ore, coal, flue dust → Ge concentrate → GeCl₄ → GeO₂ → First reduction metal → Intrinsic Ge metal → Single-crystal Ge

Processing steps:
- Grinding, magnetic separation, flotation
- Chlorination, distillation, purification
- Pyrometallurgy
- Hydrometallurgy

Uses:
- Optical casting
- Infrared lenses
- Solar cells
- X-ray monochromator crystals
- Fibre optics
- PET catalysts
- BGO
- Medicine
- Phosphors
- Alloys, compounds

Processing step: Ge scrap → Optical casting
<table>
<thead>
<tr>
<th>Market sector</th>
<th>End use</th>
<th>Prognosis 2030</th>
<th>Ge product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre optics</td>
<td>30 %</td>
<td>+5-7% p.a.; <strong>&gt;200 t in 2030</strong></td>
<td>GeO$_2$ dopant in glass fibres</td>
</tr>
<tr>
<td>Infra-red optics</td>
<td>25 %</td>
<td>Increasing demand</td>
<td>Polycrystalline + single crystals; GeO$_2$ as component of glasses in camera lenses</td>
</tr>
<tr>
<td>Polymerization catalysts</td>
<td>25 %</td>
<td>Decreasing trend</td>
<td>GeO$_2$</td>
</tr>
<tr>
<td>Electronics</td>
<td>15 %</td>
<td>Increasing, rates uncertain</td>
<td>Si-Ge-based chips</td>
</tr>
<tr>
<td>Semiconductors</td>
<td></td>
<td>Increasing demand</td>
<td>Ge doped with Sb, As, P (n-type); Al, B, Ga (p-type)</td>
</tr>
<tr>
<td>Diodes</td>
<td></td>
<td>32% increase 2009-2014 (Ge Corp estimate)</td>
<td>Ge substrate for high brightness LEDs</td>
</tr>
<tr>
<td>Transistors</td>
<td></td>
<td>Increasing demand</td>
<td>Si-Ge bipolar transistors; Si-on-insulator technology</td>
</tr>
<tr>
<td>Solar cells</td>
<td></td>
<td>Increasing demand</td>
<td>Polished Ge wafers for multilayer solar cells (40% efficiency)</td>
</tr>
<tr>
<td>Radiation detectors</td>
<td>5 %</td>
<td>Unknown</td>
<td>Single crystals of ultra-pure Ge</td>
</tr>
<tr>
<td>Superconductors</td>
<td></td>
<td>Increasing</td>
<td>Melting Ge with metals (Nb$_3$Ge)</td>
</tr>
<tr>
<td>Medicine</td>
<td></td>
<td>Unknown</td>
<td>Ge-organic compounds</td>
</tr>
</tbody>
</table>
Historical Germanium Production

Data: USGS, BGR, BGS
The “Metal Wheel”

Major metal

By-products

With special infrastructure

Limited infrastructure

No infrastructure → tailings

Sulfidic ores

Oxidic ores

Sulfidic + oxidic ores

By-products

With special infrastructure

Limited infrastructure

No infrastructure → tailings

Sulfidic ores

Oxidic ores

Sulfidic + oxidic ores
Lifetime of reserves: known reserves / annual production

- **Rare earths**: Reserves 706 years, Reserve base 1,246 years
- **Vanadium**: Reserves 192 years, Reserve base 559 years
- **Manganese**: Reserves 36 years, Reserve base 403 years
- **Cobalt**: Reserves 111 years, Reserve base 204 years
- **Iron ore**: Reserves 90 years, Reserve base 202 years
- **Bauxite**: Reserves 123 years, Reserve base 173 years
- **Tantalum**: Reserves 38 years, Reserve base 137 years
- **Nickel**: Reserves 46 years, Reserve base 100 years
- **Copper**: Reserves 36 years, Reserve base 65 years
- **Lead**: Reserves 20 years, Reserve base 43 years
- **Tin**: Reserves 18 years, Reserve base 33 years
- **Gold**: Reserves 19 years, Reserve base 43 years
- **Indium**: Reserves 19 years, Reserve base 28 years
- **Germanium**: Reserves 4.2/4.7 years

**Small lifetime based on US reserves only!**

- Reserve base of China:
  - 3055 t Ge (Asian Metal Ltd., 2008)
  - 3782 t Ge (Xun, 2002)
  - = lifetime of 30-40 years

**Available global data:**
- = 38,000 t Ge reserves + resources
- = 380 y lifetime of known reserves and resources at 100 tpy production
Germanium: Abundance in rocks and ores

Source:
- Höll et al. 2007
- Ketris & Yudovich 2009

Background: 2 ppm
Enrichment factors 5-100
Germanium mineralogy

- ca. 30 Ge minerals occur in nature but are rare

- 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

**Tsumeb**

- Germanite
- Tennantite

**Kipushi**

- Reniérite
- Briartite

**Germanite**

\[ \text{Cu}_{13}\text{Fe}_2\text{Ge}_2\text{S}_{16} \]

**Reniérite**

\[(\text{Cu},\text{Zn})_{11}(\text{Ge},\text{As})_2\text{Fe}_2\text{S}_{16}\]

**Briartite**

\[\text{Cu}_2(\text{Fe},\text{Zn})\text{GeS}_4\]

**Tennantite**

\[(\text{Cu},\text{Fe},\text{Zn})_{12}\text{As}_4\text{S}_{13}\]

**Germanite ore**

- 100 µm scale

- 50 µm scale
<table>
<thead>
<tr>
<th>Class</th>
<th>Type</th>
<th>Past production</th>
<th>Potential</th>
<th>Typical ore grade Ge (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Volcanic-hosted Cu-Zn</td>
<td>low</td>
<td>medium</td>
<td>&lt;=100 (-300)</td>
</tr>
<tr>
<td>2.1</td>
<td>Porphyry Cu-Mo-Au</td>
<td>low</td>
<td>low</td>
<td>10 - 100</td>
</tr>
<tr>
<td>2.2</td>
<td>Porphyry Sn-Ag</td>
<td>low</td>
<td>medium</td>
<td>10 - 100</td>
</tr>
<tr>
<td>3</td>
<td>Vein-type (Ag-Pb-Zn)</td>
<td>high (pre-1993)</td>
<td>low</td>
<td>100 - 1000</td>
</tr>
<tr>
<td>4</td>
<td>Sediment-hosted Zn-Pb-Cu</td>
<td>high</td>
<td>high</td>
<td>10 - 100</td>
</tr>
<tr>
<td>5.1</td>
<td>Carbonate-hosted Zn-Pb</td>
<td>high</td>
<td>high</td>
<td>10 - 1000</td>
</tr>
<tr>
<td>5.2</td>
<td>Kipushi-type polymetallic</td>
<td>high</td>
<td>medium</td>
<td>10 - 1000</td>
</tr>
<tr>
<td>5.3</td>
<td>Oxidation of 5.2 (Apex-type)</td>
<td>medium</td>
<td>low</td>
<td>100 - 1000</td>
</tr>
<tr>
<td>5.4</td>
<td>Non-sulfide Zn-Pb</td>
<td>low</td>
<td>low</td>
<td>10 - 100</td>
</tr>
<tr>
<td>6</td>
<td>Sediment-hosted stratiform Cu</td>
<td>low</td>
<td>medium</td>
<td>1 - 20</td>
</tr>
<tr>
<td>7</td>
<td>Iron oxide ores</td>
<td>none</td>
<td>low</td>
<td>10 - 50</td>
</tr>
<tr>
<td>8</td>
<td>Coal and lignite</td>
<td>medium/high</td>
<td>high</td>
<td>100 - 1000</td>
</tr>
</tbody>
</table>
Active and potential Ge producers from sulfide ore and slag

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

Smelter at Trail, B.C.
**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)

<table>
<thead>
<tr>
<th>Element</th>
<th>Bladed</th>
<th>Porous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe wt.%</td>
<td>9.0</td>
<td>3.7</td>
</tr>
<tr>
<td>Zn wt.%</td>
<td>57.3</td>
<td>62.5</td>
</tr>
<tr>
<td>Ge ppm</td>
<td>860</td>
<td>218</td>
</tr>
<tr>
<td>Cd ppm</td>
<td>2887</td>
<td>2873</td>
</tr>
<tr>
<td>As ppm</td>
<td>653</td>
<td>336</td>
</tr>
</tbody>
</table>
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

Fe-Zn slag
500 ppm Ge

Germanite

Ge ores grading >1 % Ge

D-E-R-A
Deutsche Rohstoffagentur
Bundesanalt für Geowissenschaften und Rohstoffe
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

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

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

- **All resources**: ca. 35,600 t
- **Sulfide ores and slags**: ca. 11,000 t
- **Coal**: ca. 24,600 t
<table>
<thead>
<tr>
<th>Deposit</th>
<th>Country</th>
<th>Type</th>
<th>Ge resources (metric tons)</th>
<th>Ge production capacity (tpa) (installed/max)</th>
<th>Current Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huize</td>
<td>China</td>
<td>Sulfide</td>
<td>600</td>
<td>10 / 30</td>
<td>production</td>
</tr>
<tr>
<td>Jinding</td>
<td>China</td>
<td>Sulfide</td>
<td>3000</td>
<td>10 / 10</td>
<td>production</td>
</tr>
<tr>
<td>Fankou</td>
<td>China</td>
<td>Sulfide</td>
<td>600</td>
<td>15 / 15</td>
<td>production</td>
</tr>
<tr>
<td>Red Dog</td>
<td>USA</td>
<td>Sulfide</td>
<td>1200</td>
<td>28 / 60</td>
<td>production</td>
</tr>
<tr>
<td>Tres Marias</td>
<td>Mexico</td>
<td>Sulfide</td>
<td>150</td>
<td>0 / 10</td>
<td>exploration</td>
</tr>
<tr>
<td>Pend Oreille</td>
<td>USA</td>
<td>Sulfide</td>
<td>300</td>
<td>0 / 50</td>
<td>dormant</td>
</tr>
<tr>
<td>Gordonsville</td>
<td>USA</td>
<td>Sulfide</td>
<td>800</td>
<td>0 / 35</td>
<td>dormant</td>
</tr>
<tr>
<td>Lubumbashi</td>
<td>DR Congo</td>
<td>Slag</td>
<td>2250</td>
<td>2 / 20</td>
<td>production</td>
</tr>
<tr>
<td>Tsumeb</td>
<td>Namibian</td>
<td>Slag</td>
<td>530</td>
<td>0 / 10</td>
<td>exploration</td>
</tr>
<tr>
<td>Lincang</td>
<td>China</td>
<td>Coal</td>
<td>1060</td>
<td>25 / 25</td>
<td>production</td>
</tr>
<tr>
<td>Wulantuga</td>
<td>China</td>
<td>Coal</td>
<td>1600</td>
<td>5 / 20</td>
<td>production</td>
</tr>
<tr>
<td>Novikovsk etc.</td>
<td>East Russia</td>
<td>Coal</td>
<td>6200</td>
<td>5 / 20</td>
<td>production</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>&gt;18,000</strong></td>
<td><strong>100 / 305</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Proportion of coal to sulfide + slag</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>35 / 21 %</strong></td>
<td></td>
</tr>
</tbody>
</table>
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 GeO₂ 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 | ca. 40 - 80 t / year |
| Improved recovery technologies |

#### Situation alarming

**High country concentration, country risk (China)**

#### Production:

By-product from Zn-Cu-ores (USA, China) and coal (China, Russia)
Thank you


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