The oxidized ores of the Main Sulfide Zone, Great Dyke, Zimbabwe: Turning resources into minable reserves – mineralogy is the key!

Thomas Oberthür
Frank Melcher, Malte Junge, Marek Locmelis, Peter Buchholz, Herwig Marbler, Dennis Kraemer, Gila Merschel, and Michael Bau
Outline of Talk

The Great Dyke of Zimbabwe

Main Sulfide Zone, Great Dyke

Pristine ores
- Geochemistry
- Mineralogy

Oxidized ores
- Geochemistry
- Mineralogy
- Metallurgical options
Hartley Mine
Ngezi Mine
100 km
Mafic Sequence
Ultramafic Sequence
Stratigraphy of the Great Dyke

Mafic Sequence, + 1150 m
- Gabbros, Norites, Gabbronorites

Ultramafic Sequence, + 2300 m
- Dunites/Serpentinites, Harzburgites, Olivine-bronzitites, Pyroxenites, Websterite
- Chromitites

Bronzitite succession
- upper
- middle
- lower

Dunite succession
- MSZ

BGR Bundesanstalt für Geowissenschaften und Rohstoffe
GEOZENTRUM HANNOVER
Great Dyke, Zimbabwe
Main Sulfide Zone, Mimosa Mine, Great Dyke

Vertical zonation or “offsets“ (Prendergast; Wilson)

Sulfide, Ni, Cu

Base metal subzone

PGE subzone

Pt

Pd

pyroxenite
Platinum-group minerals (PGM)

Mimosa MIM-603

Hartley, SD-04

Hartley Mine GD-11-D

MoS₂ (contains up to 3000 ppm Pd !)

cpy

po

sperrylite

moncheite

cooperite
Grains from concentrates (electric pulse, Univ. Leoben)

Pt-Fe alloy

(Pt,Pd)(Te,Bi)$_2$

PtS

PtAs$_2$
PGM - Main Sulfide Zone

- Moncheite
- Maslovite
- Merenskyite
- Michenerite
- Kotulskite

- Cooperite - Braggite
- Sperrylite
- Rh-Ir-Ru-Pt-sulfarsenides
- Laurite
- Pt-Fe-alloy
- "PtSnS"

~ 70 % are Pt-minerals !
PGM by dominant PGE (%)
Regional variation – PGM proportions – Great Dyke

- **Hartley**: (Pt,Pd)-bismuthotellurides
- **Mhondoro**: Pt-Fe alloys
- **Ngezi**: others
- **Unki**: (PGE)-sulfarsenides
- **Mimosa**: PtAs₂

**Comparative Analysis**

- Bi,Te > As
- As > Bi,Te

- Great Dyke PGM Proportions:
  - Hartley: (Pt,Pd)-bismuthotellurides
  - Mhondoro: Pt-Fe alloys
  - Ngezi: others
  - Unki: (PGE)-sulfarsenides
  - Mimosa: PtAs₂
Pd in pentlandite (ppm)  

example: Unki

~ 80 % of the Pd is hosted in pentlandite!
Distribution of PGE

PGE are bimodally distributed

- **Pt, Os, Ru**: discrete PGM
- **Pd, Rh, Ir**: in sulfides (mainly pentlandite)
**PGM / PGE in the exogenic cycle**

<table>
<thead>
<tr>
<th>PGM</th>
<th>MSZ pristine</th>
<th>MSZ oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pt,Pd)(Bi,Te)*</td>
<td>30-70%</td>
<td></td>
</tr>
<tr>
<td>PtAs₂</td>
<td>~ 25%</td>
<td></td>
</tr>
<tr>
<td>(Pt,Pd,Ni)S</td>
<td>~ 80% of Pd total</td>
<td>?</td>
</tr>
<tr>
<td>Pd in pentlandite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Oxide ores

- Great Dyke ~ 250 Mt of resources!
- Bushveld some 100 Mt
  (Platreef, MR, UG-2)

- Characterization of the mineralogy of the PGE
- Development of new processing technologies
  ("conventional“ PGE recovery only ≤ 30% !)
Oxide ores, Hartley Platinum Mine

Resources: ~ 250 Mt of ore!
Hartley Mine, Zimbabwe
Sampling “Old Wedza“ (Mimosa)
Martin Prendergast’s outcrop
Oxide Ores

- Geology
- Geochemistry
- Mineralogy
Geochemical trends: Sulfide ores → oxide ores

Pt/Pd = 1.28  (n=12)

Pt/Pd = 2.43  (n=9)
MSZ: gains/losses during weathering

After Gresens (1967). Al = constant
Oxide Ores

- Geology
- Geochemistry
- Mineralogy
NGEZI (Tiefenprofil)

distance [m] to MSZ beacon

- **MHR194**
  - 0.0
  - 2.5 Base metal interval
  - 6.5
  - 2239
  - 2800 = ppb Pt (on Pt peak)

- **MHR195**
  - 1.0
  - 5.0 PGE interval
  - 1441
  - 2490

- **MHR196**
  - 5.5
  - 9.0
  - 3880
  - 2146

- **MHR197**
  - 10.0
  - 9.5
  - 4760
  - 1886

- 25 m depth

2239 = ppb Pt (average of 8 samples in PGE interval)
<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth metres</th>
<th>Degree of oxidation</th>
<th>PtAs$_2$</th>
<th>(Pt,Pd) S</th>
<th>Pt-Fe alloys</th>
<th>(Pt,Pd) (Bi,Te)</th>
<th>$\Sigma$ PGM</th>
<th>Oxide minerals</th>
<th>Sulfides</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHR 194</td>
<td>4-4.5</td>
<td></td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>Goethite, chromite</td>
<td>None</td>
</tr>
<tr>
<td>MHR 195</td>
<td>6.5-7</td>
<td></td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>5</td>
<td>Goethite, hematite, magnetite, chromite</td>
<td>None</td>
</tr>
<tr>
<td>MHR 196</td>
<td>10-10.5</td>
<td></td>
<td>9</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>11</td>
<td>Goethite, hematite, magnetite, rutile</td>
<td>Sparse relicts in silicates</td>
</tr>
<tr>
<td>MHR 197</td>
<td>15-15.5</td>
<td></td>
<td>4</td>
<td>12</td>
<td>-</td>
<td>28</td>
<td>44</td>
<td>Magnetite, chromite</td>
<td>Po, pn, cpy, py. Incipient oxidation at rims</td>
</tr>
</tbody>
</table>
Relict PGM

Sperrylite BSE image polished section

Sperrylite SEM image

Cooperite SEM image

HOP-102

HOP-103
Relict sulfides

Relict pentlandite:
up to 6500 ppm Pd
up to 450 ppm Pt

127 ppm Pd
Replacement of (Pt,Pd)(Bi,Te)*

coop
mich
Pt-Fe

10 µm

Replacements

mer

25 µm

Ngezi Adit A (5711b)
HOP-206 (5910a)
PGE - “Oxides“
Ngezi Mine

Complete replacements
(or neoformations ?)

Ngezi Adit A (both 5711b)
PGE in FeOOH, Mn-Co-OH, smectites

Mimosa
**Mimosa**

\[ \text{Mn-Ni-Co-OH}_x = 200-400 \text{ ppm Pt} \]

FeOOH = 50-80 ppm Pd

PGE in FeOOH and in Mn-Co-OH

\( \text{Pt}(\text{Fe?}) < 1 \mu m \)

\( \text{(Pd,Pt)} < 1 \mu m \)

\( \text{Pt}_x \text{-neoformation?} \)
Pt and Pd in Mn-Co and Fe-hydroxides

Hydroxides

Pt-bearing Fe hydroxides Mimosa

Pt ppm

Pd ppm

Mn-Co hydroxides Mimosa

Mn-Co hydroxides Hartley

Mimosa and Hartley

Mimosa

Hartley
Mineralogy of PGE/PGM in oxide ores

1. Relict PGM
2. Relict sulfides
3. PGE-oxides/hydroxides replacing PGM
4. Pt$_x$ (neoformation)
5. PGE in FeOOH
6. PGE in Mn-Co-OH
7. PGE in silicates (smectites)

Mineralogical balance?
<table>
<thead>
<tr>
<th></th>
<th>MSZ</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>sulfide ores</td>
</tr>
<tr>
<td></td>
<td></td>
<td>bimodal</td>
</tr>
<tr>
<td>1) discrete PGM</td>
<td></td>
<td>PtAs₂ &amp; (Pt,Pd,Ni)S (Pt,Pd)(Bi,Te)*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ptₚ (neoformation)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt &gt; Pd in FeOOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt &gt; Pd in Mn-Co-OH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd &gt; Pt in smectites</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 95%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 25%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized ores</td>
</tr>
<tr>
<td></td>
<td></td>
<td>polymodal</td>
</tr>
<tr>
<td>2) Pt in pn and py</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 75%</td>
</tr>
</tbody>
</table>
## Pd distribution

<table>
<thead>
<tr>
<th></th>
<th>MSZ</th>
<th>oxidized ores</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>sulfide ores</strong></td>
<td><strong>bimodal</strong></td>
<td><strong>polymodal</strong></td>
</tr>
<tr>
<td><strong>1)</strong> discrete PGM</td>
<td>(Pd,Pt,Ni)S</td>
<td>PGE - “oxides“</td>
</tr>
<tr>
<td></td>
<td>(Pd,Pt)(Bi,Te)*</td>
<td>Pt &gt; Pd in FeOOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt &gt; Pd in Mn-Co-OH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd &gt; Pt in smectites</td>
</tr>
<tr>
<td></td>
<td>~20%</td>
<td>~10%</td>
</tr>
<tr>
<td><strong>2)</strong> Pd in pentlandite</td>
<td></td>
<td>~40%</td>
</tr>
<tr>
<td></td>
<td>~80%</td>
<td>ca. – 50%</td>
</tr>
</tbody>
</table>

* ~ indicates approximate percentages.
### PGM / PGE in the exogenic cycle

<table>
<thead>
<tr>
<th>PGM</th>
<th>MSZ pristine</th>
<th>MSZ oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pt,Pd)(Bi,Te)*</td>
<td>30-70%</td>
<td></td>
</tr>
<tr>
<td>PtAs$_2$</td>
<td></td>
<td>~ 25%</td>
</tr>
<tr>
<td>(Pt,Pd,Ni)S</td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>Pd in pentlandite</td>
<td>~ 80% of Pd$_{\text{total}}$</td>
<td></td>
</tr>
</tbody>
</table>

*Note: Bi and Te represent bismuth and tellurium respectively.*
# Metallurgical options for oxide ores

<table>
<thead>
<tr>
<th>Method</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grainger Bros. (1926)</td>
<td>Bulk - Gravitation</td>
</tr>
<tr>
<td>Hartley Mine (1997-99)</td>
<td>Bulk - Flotation</td>
</tr>
<tr>
<td>TML Process BHP – lab scale (1992/1994)</td>
<td>Bulk – Roasting (300-425°C) Br° in NaBr in H₂SO₄ leach (70°C, 2h) CIP</td>
</tr>
</tbody>
</table>

**problems:** costs of chemicals; aggressive acids; environmental issues

| Evans (2002) | Bulk – various/hydrometallurgy – pyrometallurgy (ConRoast) | ? |

---

*Note: H₂SO₄ is sulfuric acid.*
Metallurgical options for oxide ores

BGR – (1) Establish *mineralogical balance* of PGE in the ores
- (2) Metall. tests → *mechanical pre-concentration* (?)

Step-wise crushing & milling
Electric pulse disintegration
Sieving
Gravity separation
Magnetic separation
Preconcentration
Selective leach

NO
Metallurgical options for oxide ores

BGR – previous work
Preconcentration
Selective leach

Current work: Total leach experiments (JU Bremen)
- hydrometallurgy -
(1) one-step leach using siderophores: < 1% Pt recovery
(2) two-step leach, inorganic acids + siderophores, unbuffered:
   20 – 40 % Pt recovery
(3) Bio-leaching (ongoing work, BGR labs)
(4) Inorganic acids – ongoing work – BGR/DERA + JU Bremen
Conventional processing of oxidized PGE ores problematic due to:

- missing BM sulfide association (Oberthür et al., 2013)
- Occurrence of naturally-floating gangue (Becker et al. 2014)
- Polymodal distribution of PGE (Oberthür et al., 2013)

Concentrate dilution; 15-30% Recovery

Therefore

Hydrometallurgical leaching experiments with organic and inorganic lixiviant (Jacobs University Bremen, Germany)
Leaching experiments with siderophores (biologically produced organic ligands)

Siderophores / Metallophores:

- low molecular weight organic molecules
- exuded by plants (phytosiderophores) and bacteria (microbial siderophores) to cope with nutrient deficiency or toxicity in natural systems
- In modern environments mainly produced to bind and mobilize Fe(III), which is needed as a micronutrient

But: High affinity for platinum and palladium
Leaching experiments with siderophores (biologically produced organic ligands)

**Oxidized MSZ** (Great Dyke):
- Pt recovery up to ~80%
- Selective leaching possible
- Low Pd and Ni mobilization

**Oxidized Platreef** (Bushveld):
- Very low recoveries irrespective of leaching time, reagent concentrations, preleach, etc.

Siderophore experiments demonstrate principal viability of bioleaching (leaching with biogenic compounds) for the treatment of oxidized PGE ores!
Leaching experiments with inorganic lixiviants

2B-Platinum Leach:
• Leach based on inexpensive inorganic reagents
• Initial lab-scale tests indicated very promising leaching efficiencies

Test of applicability in optimization and upscaling experiments
Nickel, Cr, Au, Pt and Pd grades of the oxidized PGE ore samples used for optimization and upscaling experiments

<table>
<thead>
<tr>
<th></th>
<th>Pt [µg/kg]</th>
<th>Pd [µg/kg]</th>
<th>Ni [mg/kg]</th>
<th>Cu [mg/kg]</th>
<th>Cr [mg/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average (n=6)</td>
<td>1184</td>
<td>924</td>
<td>2050</td>
<td>2088</td>
<td>798</td>
</tr>
</tbody>
</table>

Samples totalling 150 kg of oxidized PGE ore

Heap ore from the Mogalakwena Mine, South Africa

Heap of oxidized PGE ore: 6 mio tonnes

Samples were only crushed, one sample was milled
2B-Platinum leach:

Upscaling experiments conducted on oxidized heap ore

- Experiments at 20°C, 40°C and 80°C
- Time series: samples taken after 1h, 2h, 4h, 8h

- Upscaling experiments:
  → Up to 78% Pt and 55% Pd into solution

First results – upscaling experiments
Extraction of PGE from oxide ores by hydrometallurgical methods

Advantages:
1. Cheap and simple surface mining
2. Pt + Pd are amenable to leaching by various acids
3. Heap-leach/ tank-leach is possible
4. Inexpensive reagents
5. Good/acceptable recoveries
6. Expensive processing steps like fine-milling, flotation, smelting, matte-leaching are not needed

Challenges:
1. Heterogeneous mobilization of PGEs from oxidized PGE ores → need for better understanding of mineralogy and PGE deportment
2. **Optimization of process**
   (pre-treatment, one or multiple step leach (modified Kell process?), chemicals, temperature, etc.)

Hydrometallurgical leaching technologies may be applicable to other oxidized ore deposits
Ex Africa semper aliquid novi
....PGM grains....
weathered PGE ores - MSZ

Evans 2000
Ngezi Platinum Mine

E-W section across Trial Mine, looking N

- Low Wall (20m vertical)
- Partially/Wholly Oxidised Ore left in situ
- Backfilled access ramp to portals
- Original Ground Profile
- 3 Portals through barrier pillar
- High Wall (50m vertical)
- Fresh Sulphide Ore for trial mining by room & pillar method

BGR Bundesanstalt für Geowissenschaften und Rohstoffe
GEOZENTRUM HANNOVER
Processing of oxidized PGE ores

✓ Surficial ore - cheap mining
✓ Large portions of oxidized ore already excavated and on heaps
✓ Heap ore broken and classified

New approach:
Hydrometallurgical treatment of oxidized ores

Leaching experiments with organic and inorganic lixiviants
(Jacobs University Bremen, Germany)