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

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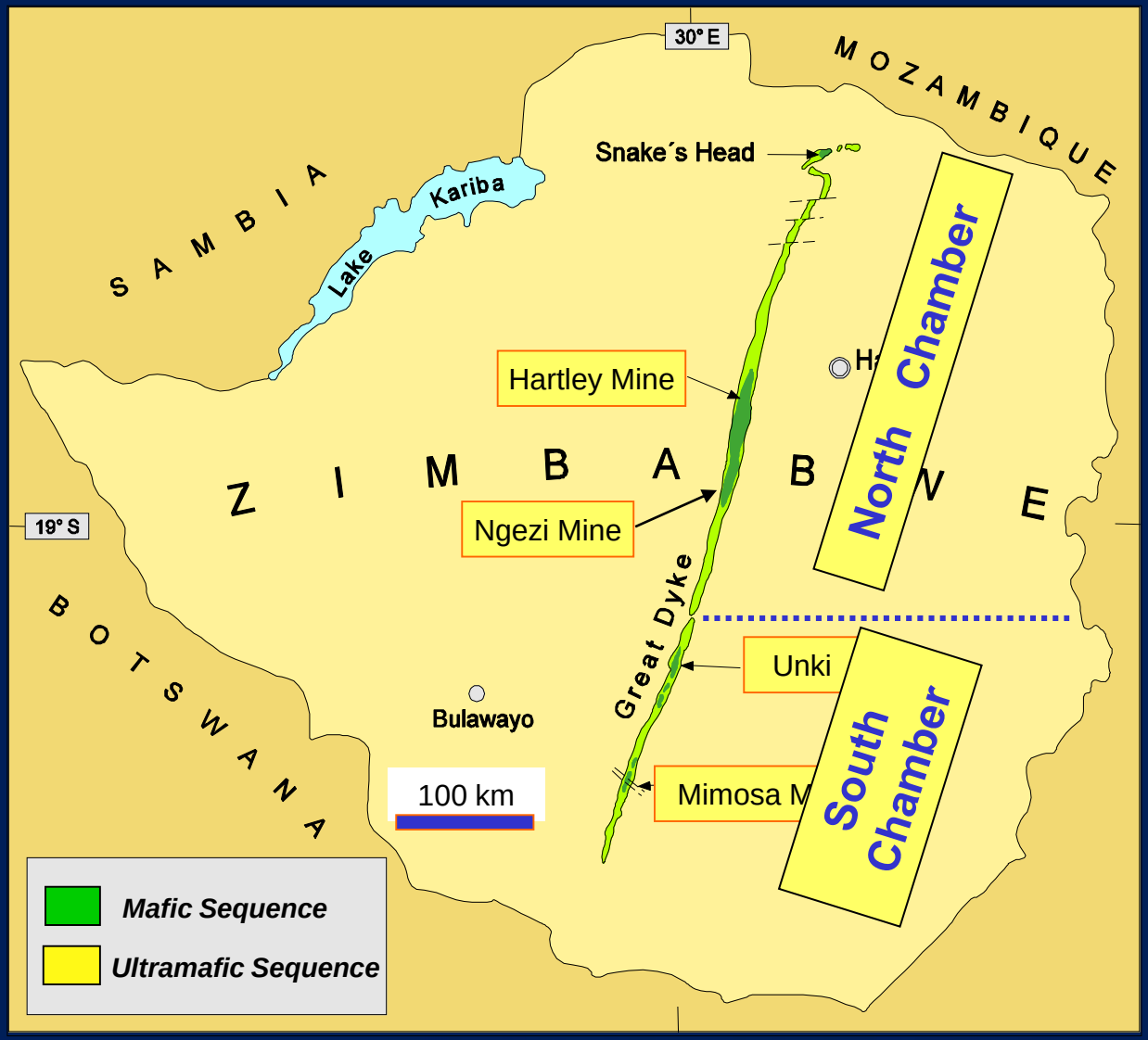
Outline of Talk

The Great Dyke of Zimbabwe

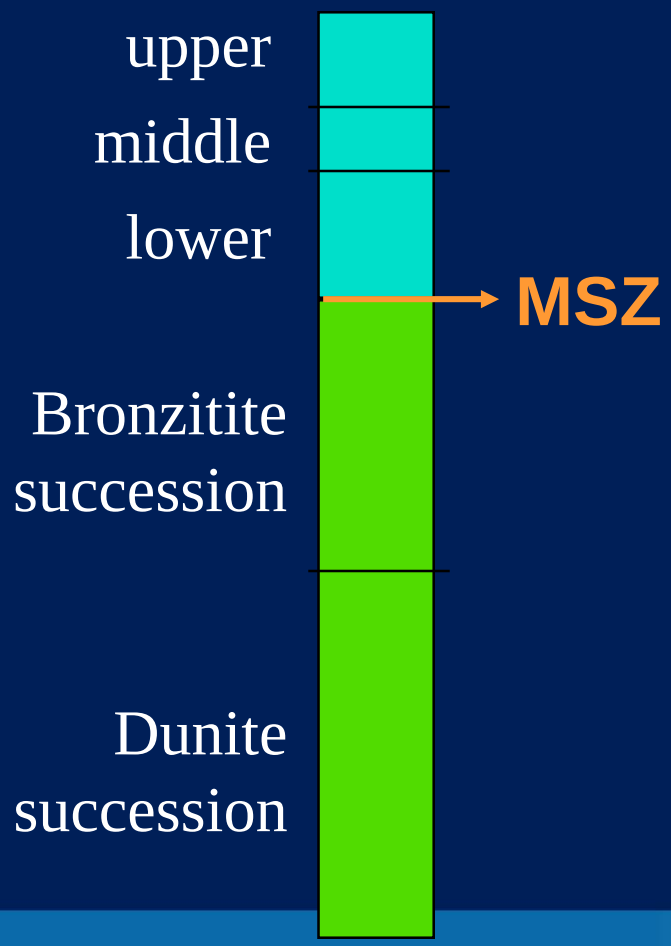
Main Sulfide Zone, Great Dyke

Pristine ores
- *Geochemistry*
- *Mineralogy*

Oxidized ores
- *Geochemistry*
- *Mineralogy*
- *Metallurgical options*



Stratigraphy of the Great Dyke



Mafic Sequence, + 1150 m

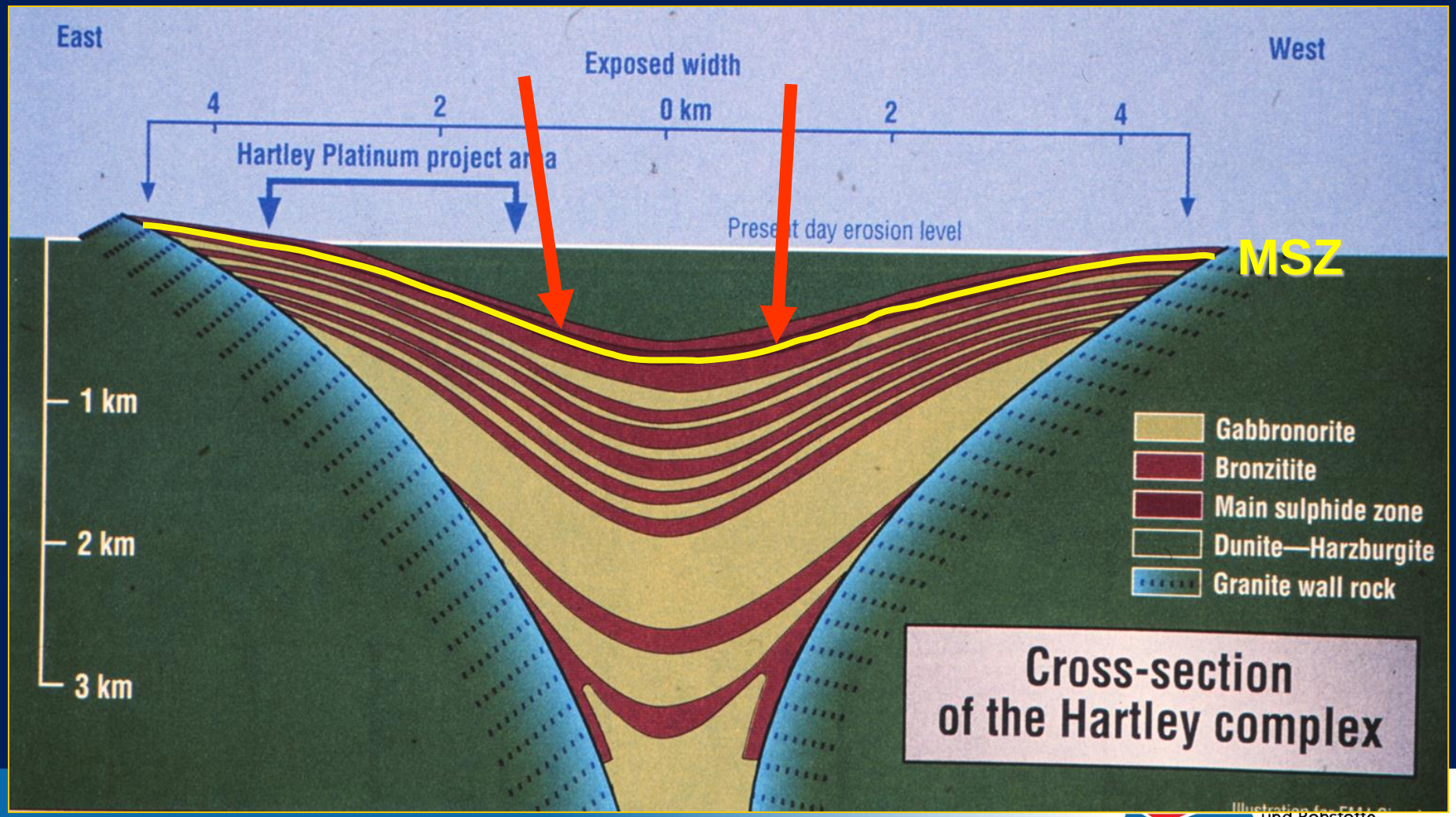
Gabbros, Norites, Gabbronorites

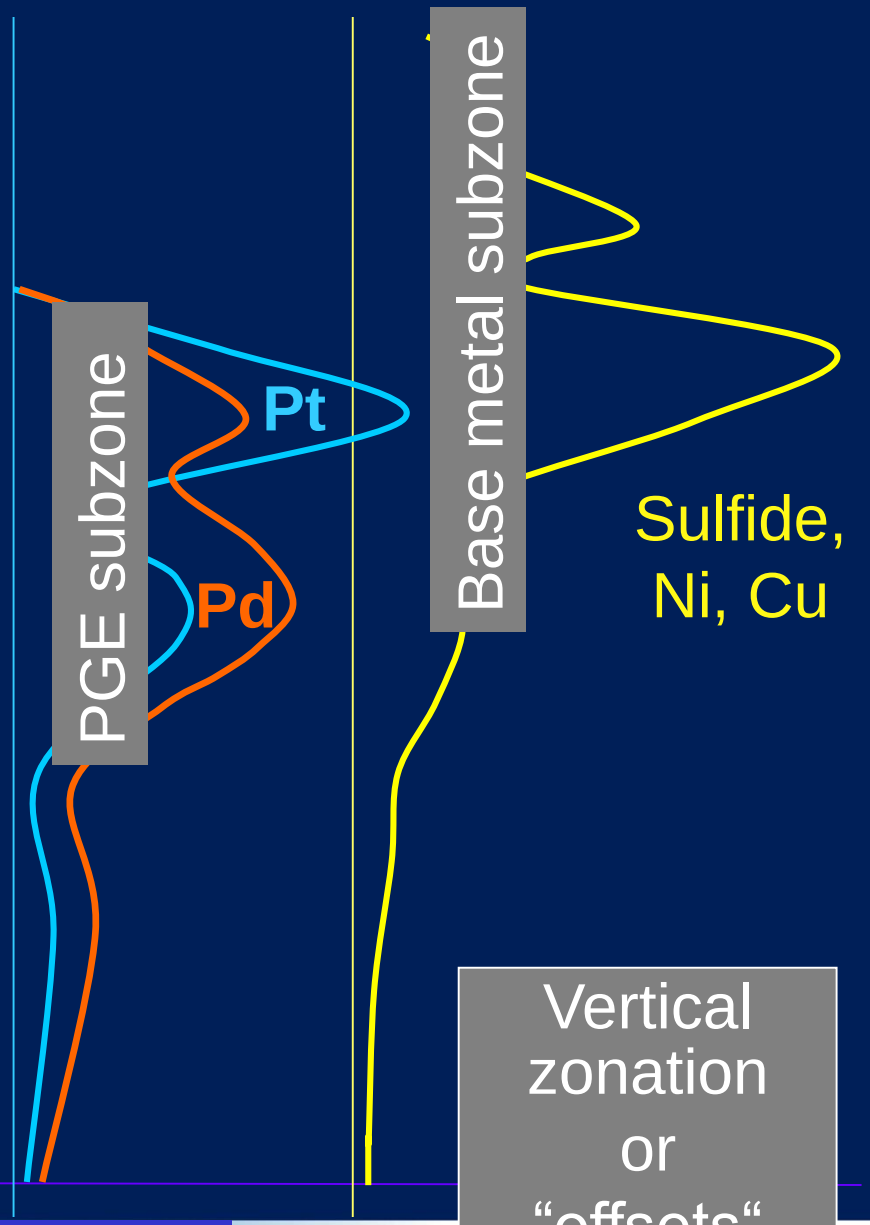
Ultramafic Sequence, + 2300 m

Dunites/Serpentinites, Harzburgites, Olivine-bronzitites, Pyroxenites, Websterite

Chromitites

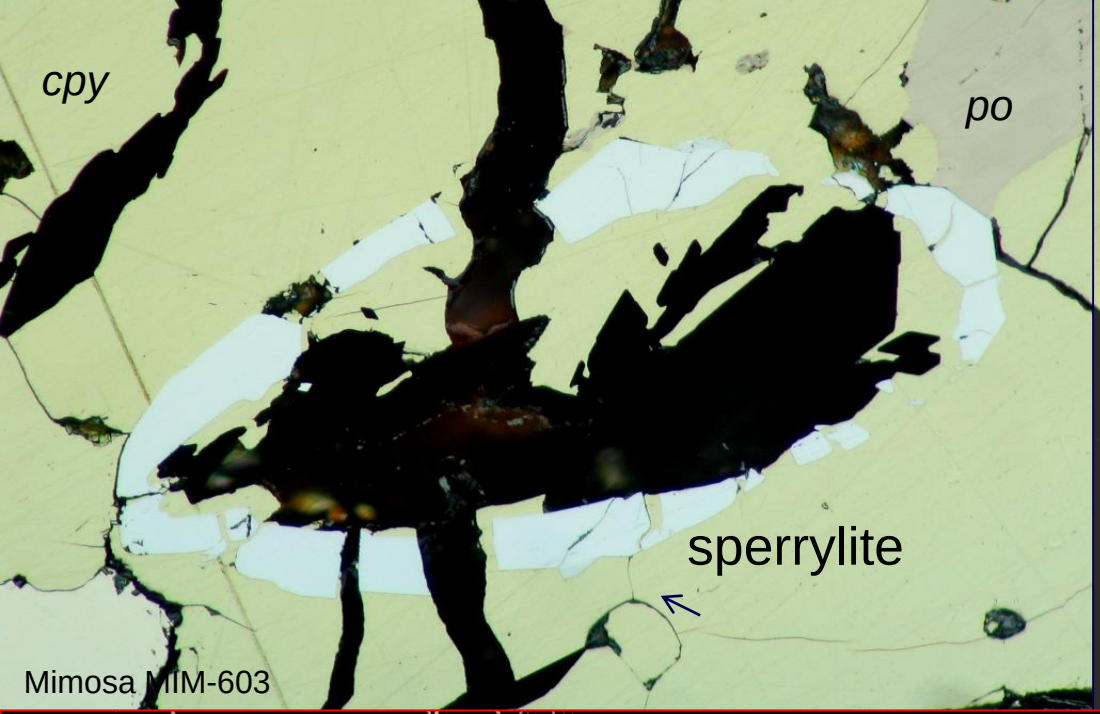
Great Dyke, Zimbabwe

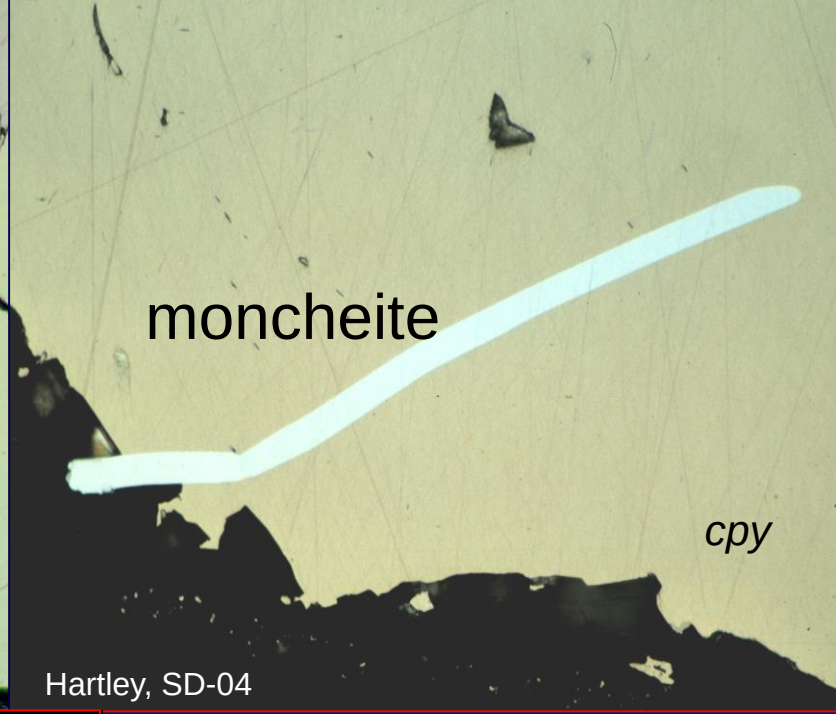


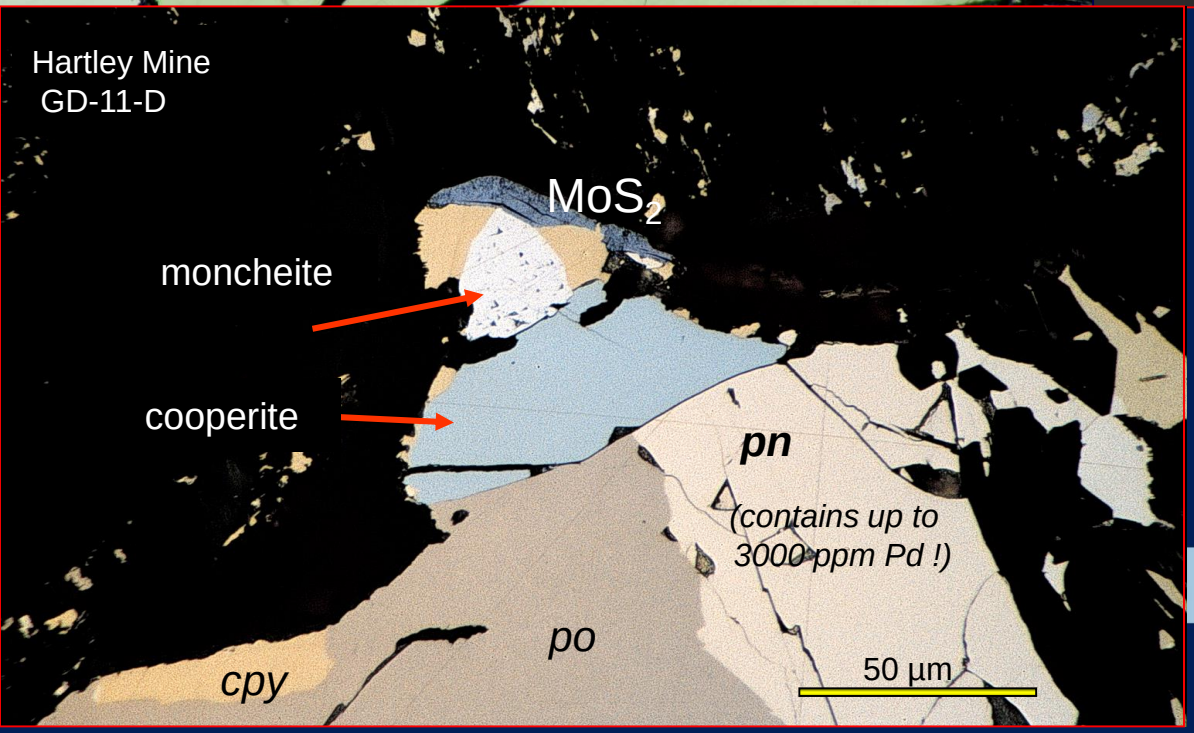


Vertical zonation or "offsets" (Prendergast; Wilson)

Main Sulfide Zone, Mimosa Mine, Great Dyke



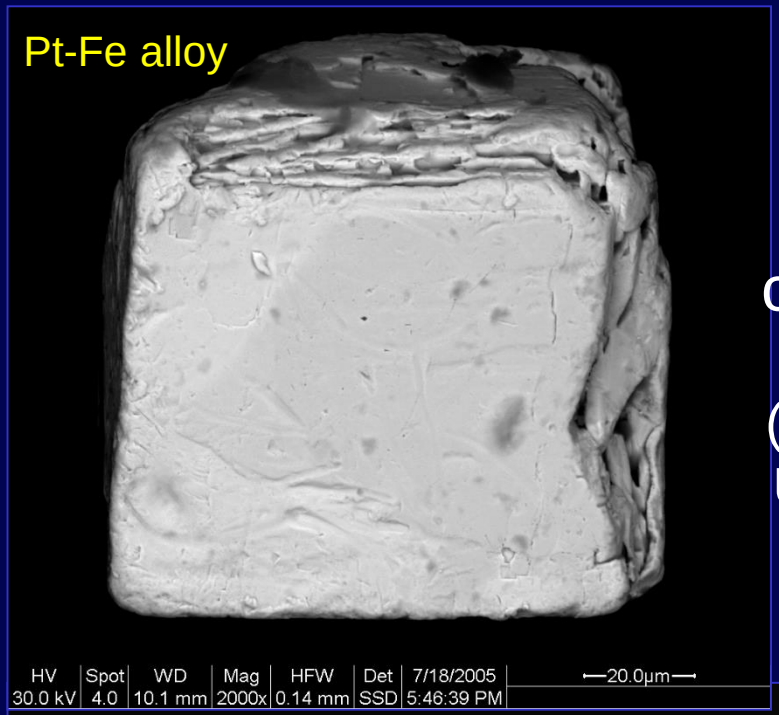


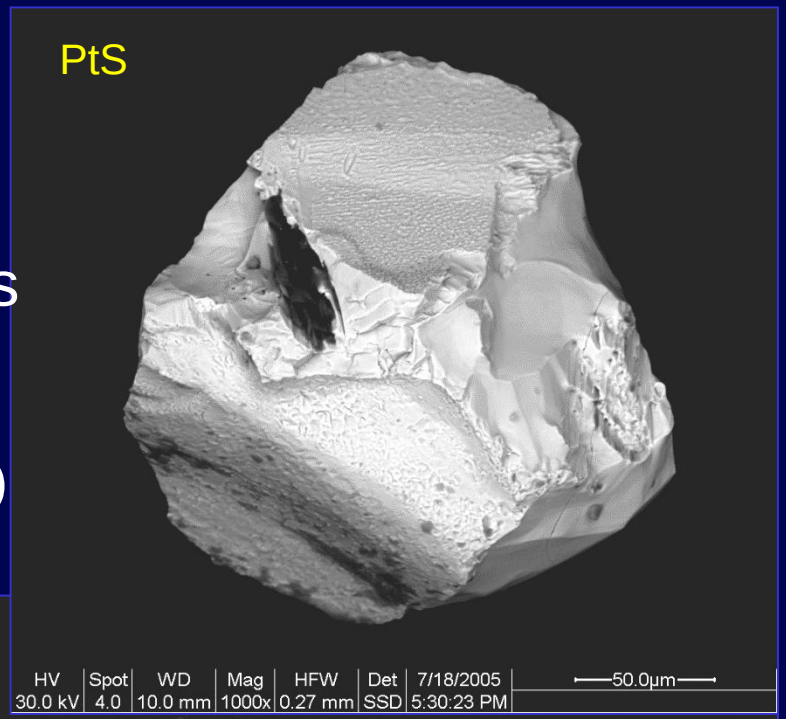


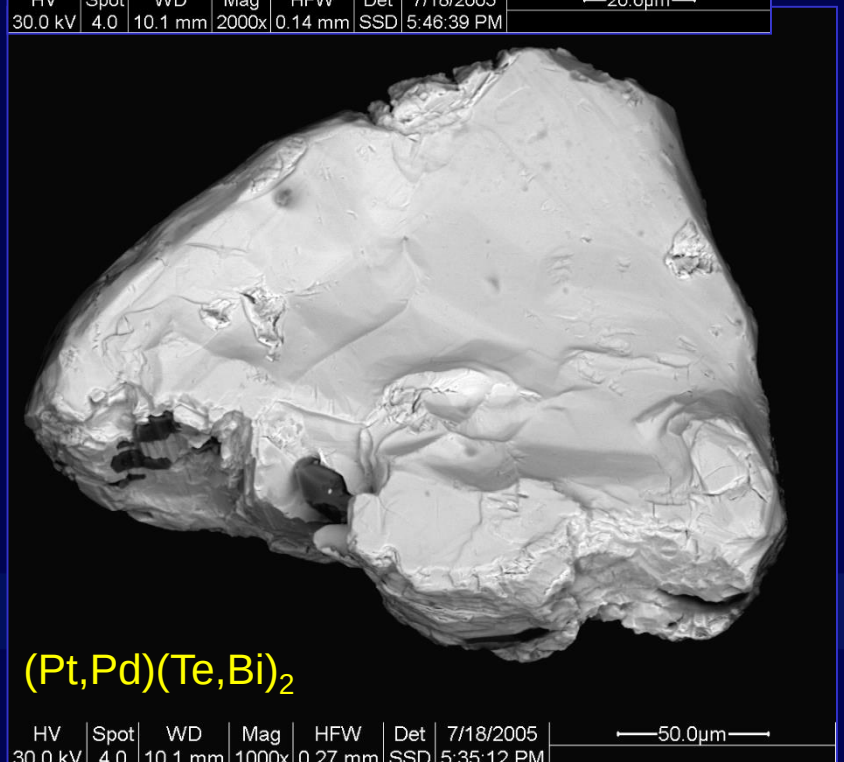
Platinum-group minerals (PGM)

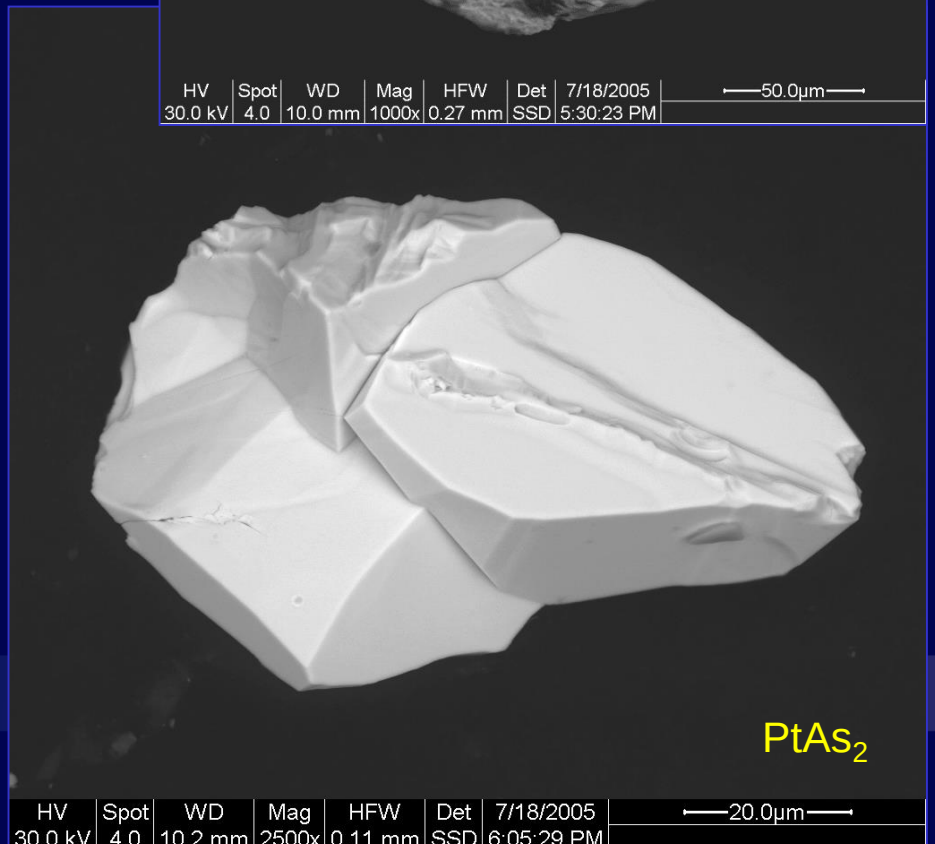
Grains from concentrates

(electric pulse, Univ. Leoben)









PGM - Main Sulfide Zone

- **Moncheite**
- **Maslovite**
- **Merenskyite**
- Michenerite
- **Kotulskite**

- **Cooperite - Braggite**

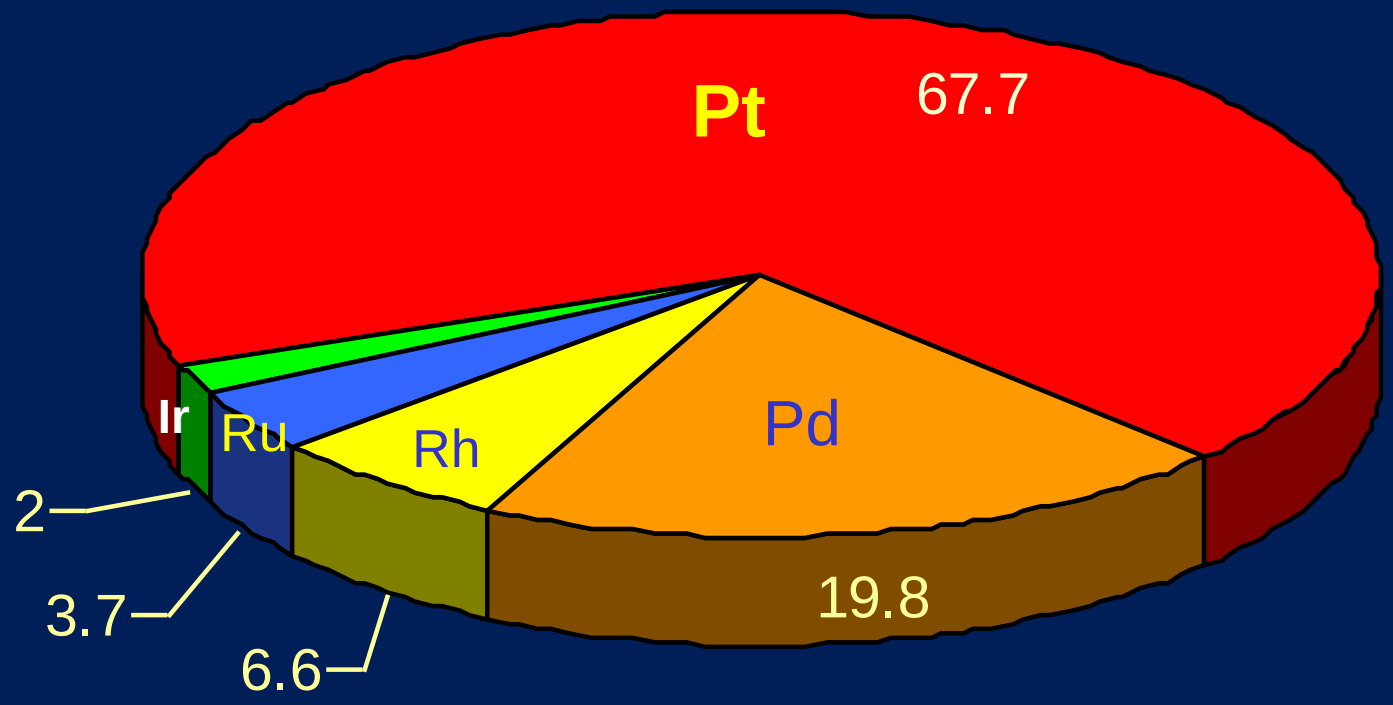
- **Sperrylite**

- Rh-Ir-Ru-Pt-sulfarsenides

- Laurite
- Pt-Fe-alloy
- "PtSnS"

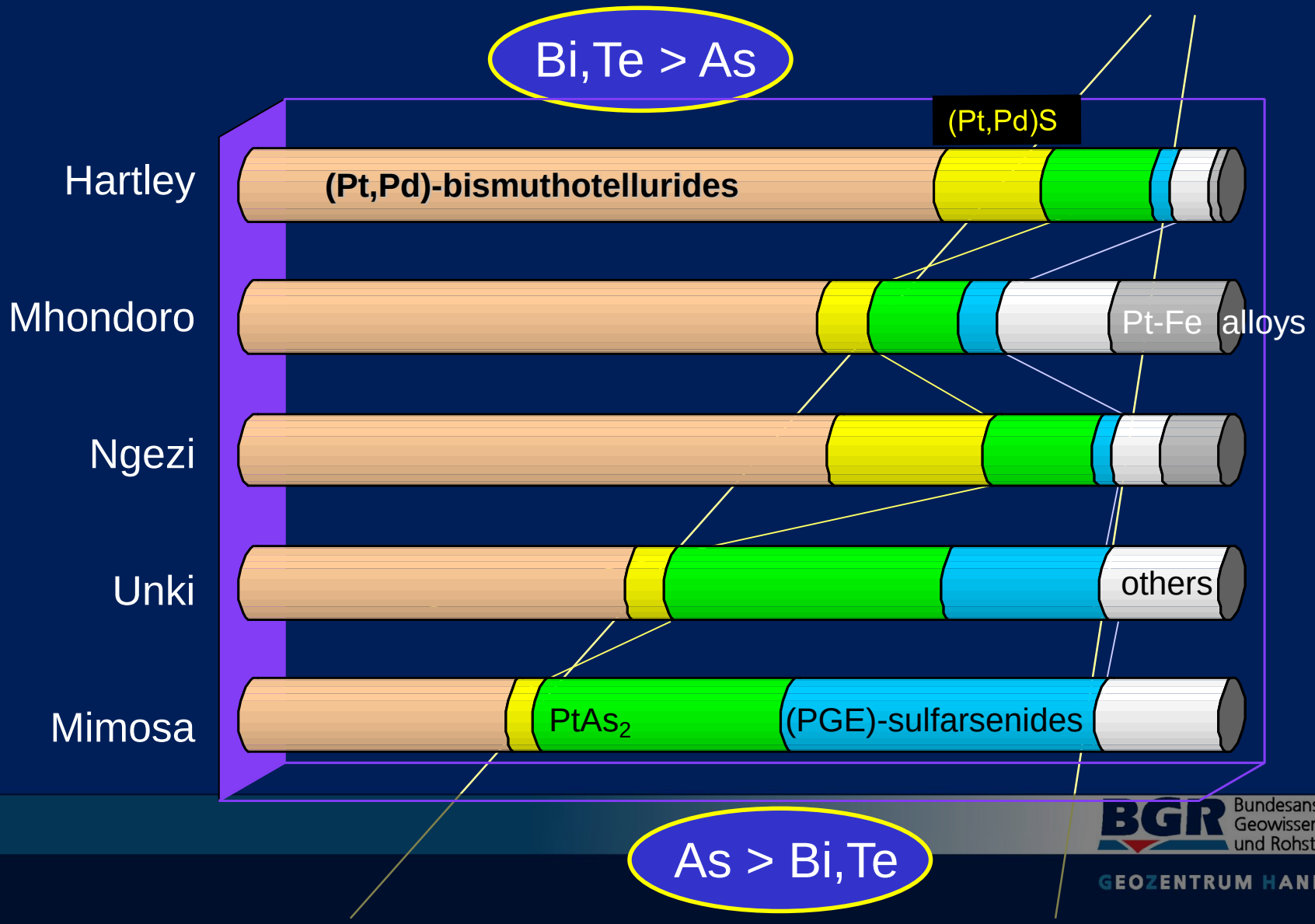
~ 70 % are Pt-minerals !

PGM by dominant **PGE** (%)

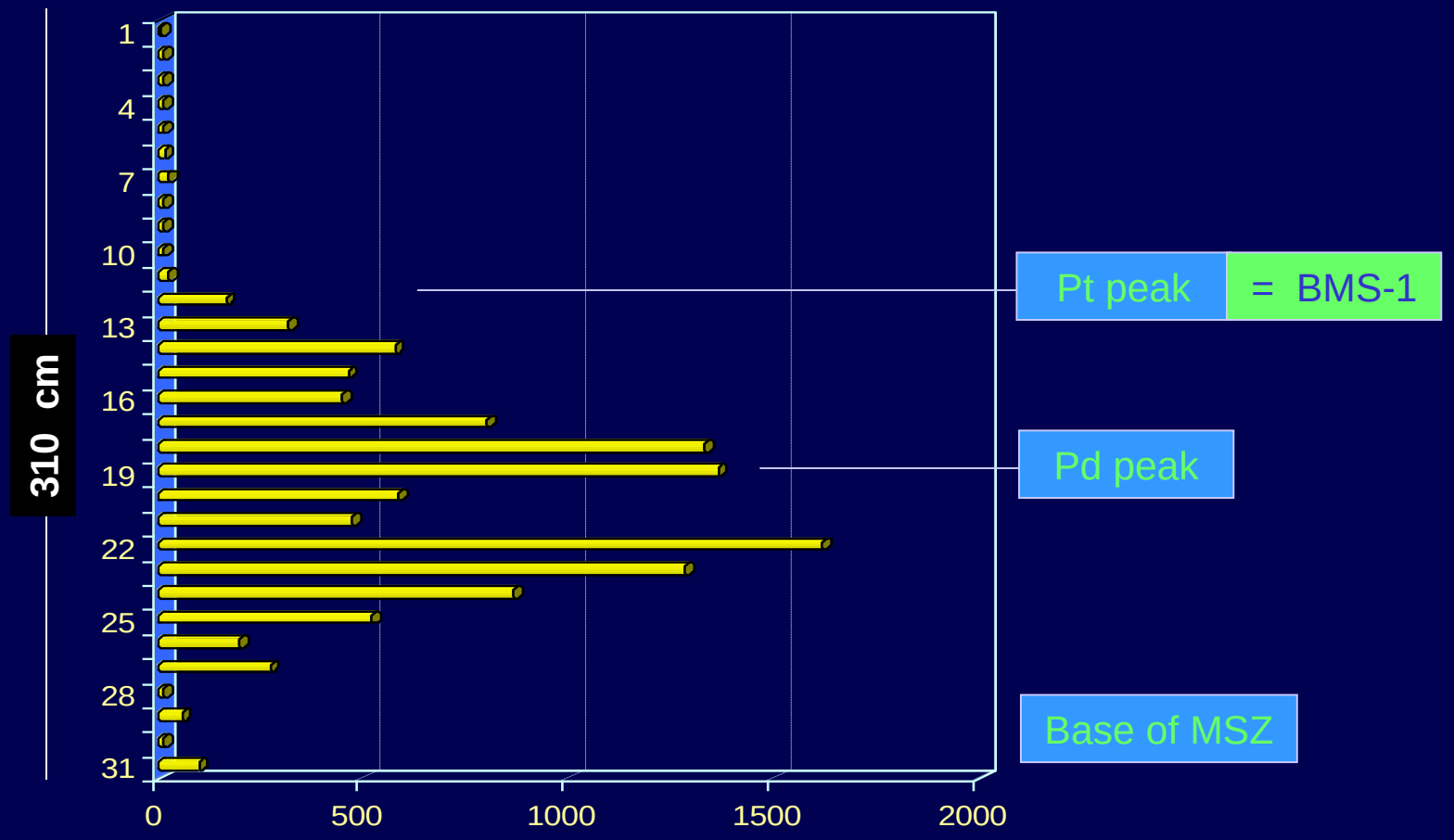


n = 781

Regional variation – PGM proportions – Great Dyke



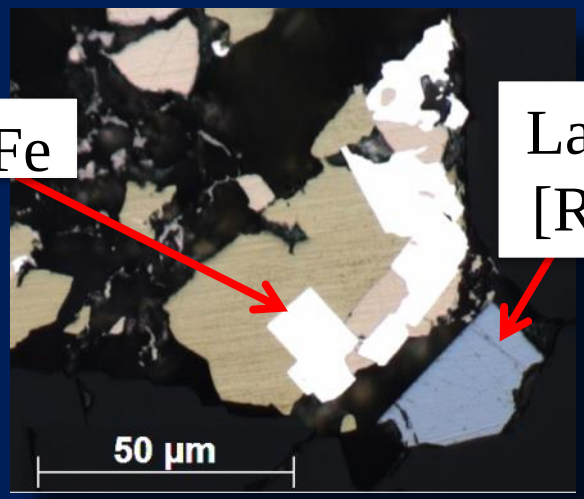
Pd in pentlandite (ppm) example : Unki

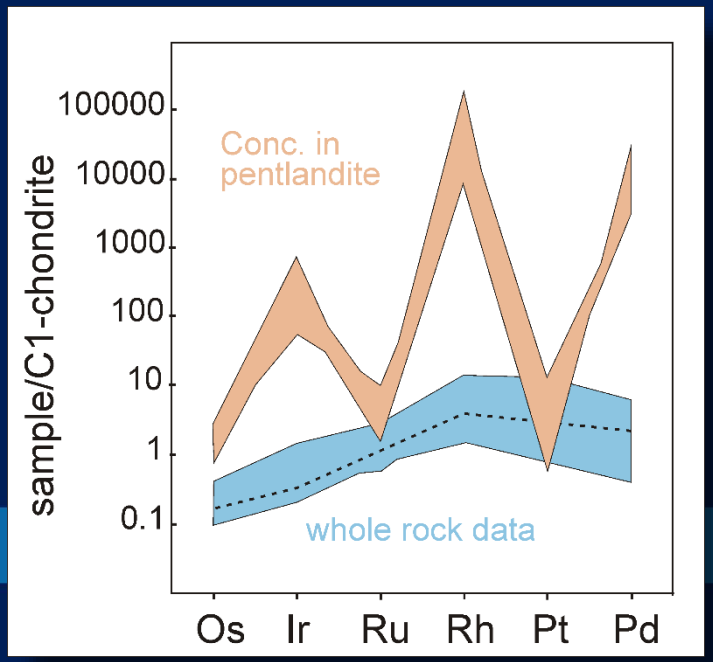


R-13

~ 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

PGM	MSZ pristine	MSZ oxidized
(Pt,Pd)(Bi,Te)*	30-70%	?
$PtAs_2$	~ 25 %	
(Pt,Pd,Ni)S		
Pd in pentlandite	~ 80% of Pd_{total}	

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% !)

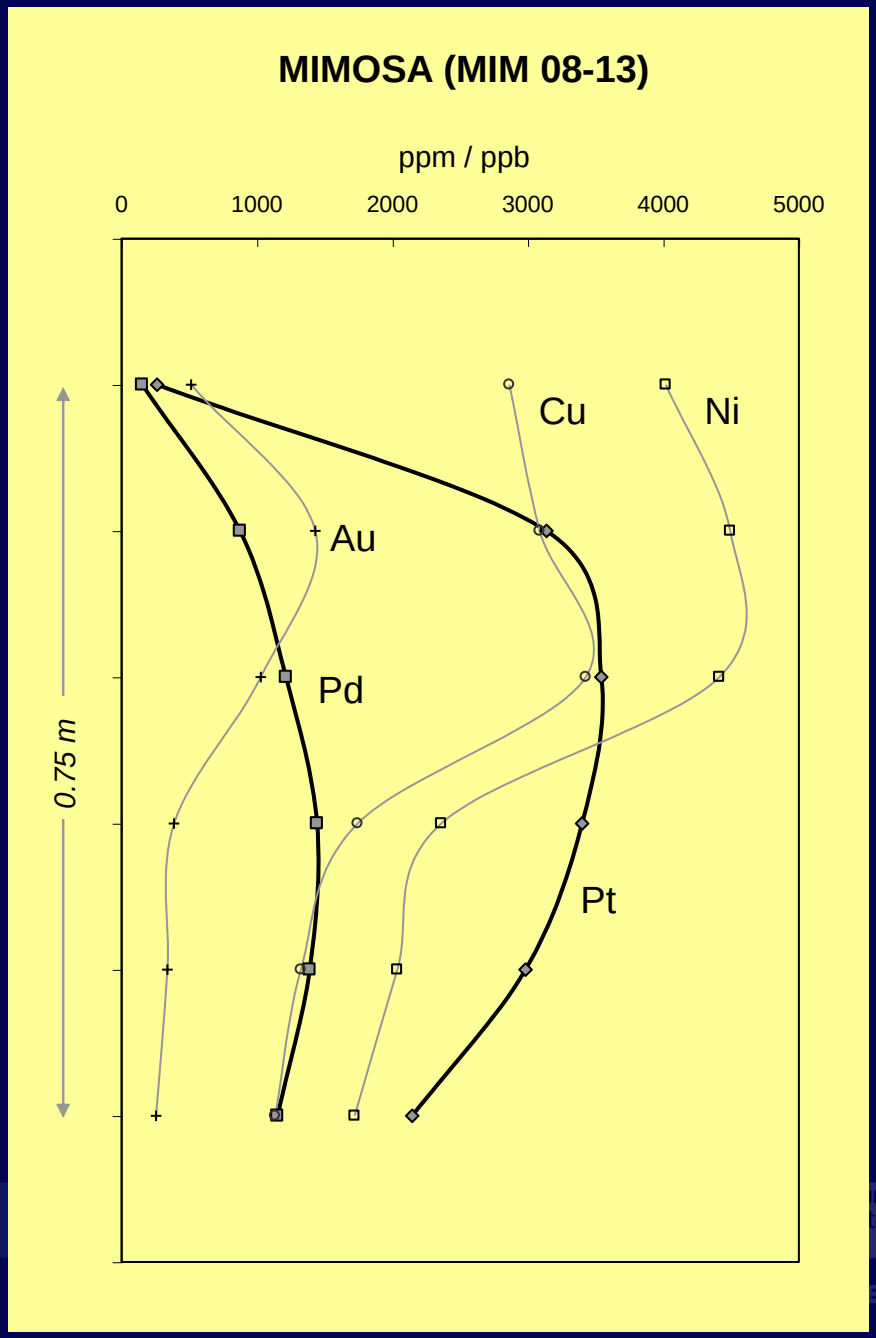
Oxide ores, Hartley Platinum Mine

Hartley Mine, Zimbabwe

Ngezi test pit

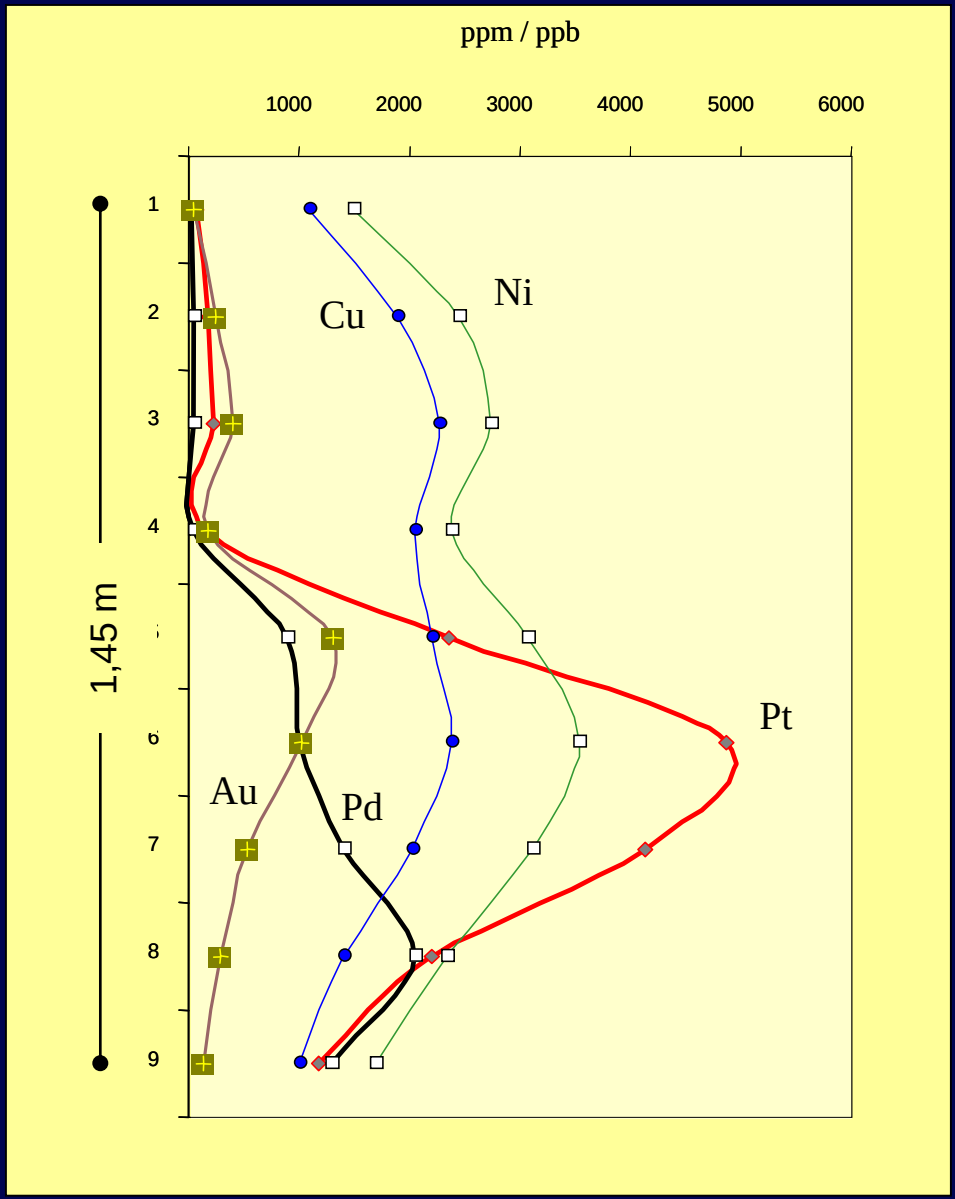
Sampling “Old Wedza“ (Mimosa)

Martin Prendergast‘s outcrop

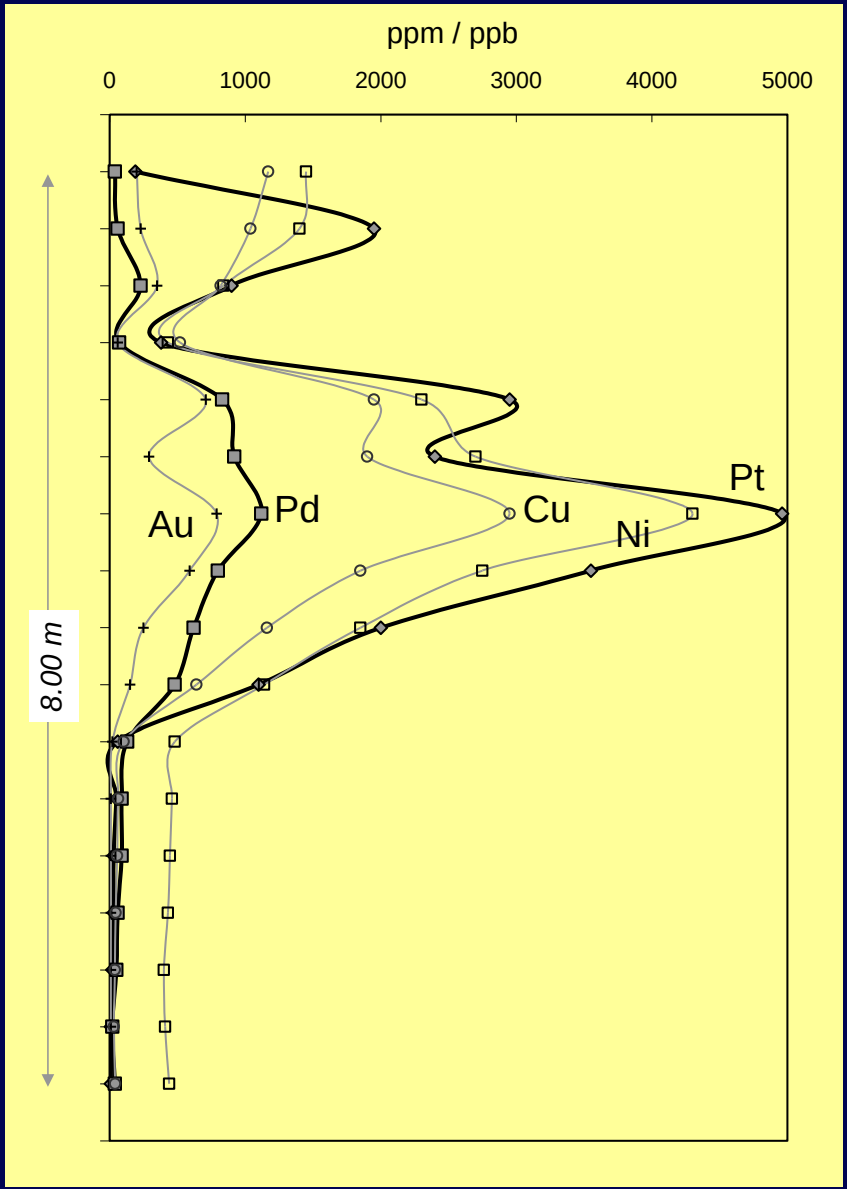


Oxide Ores

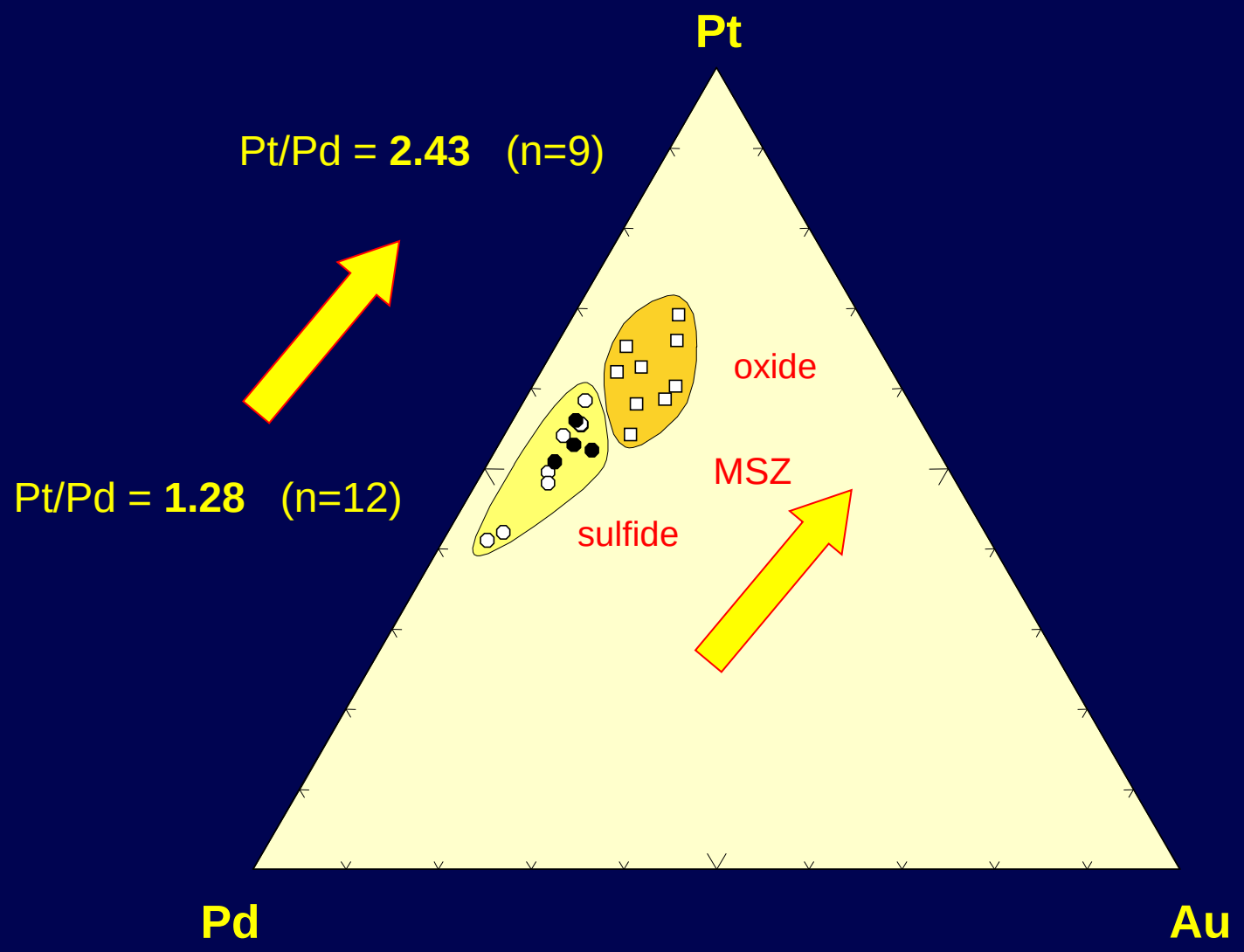
- Geology
- Geochemistry
- Mineralogy



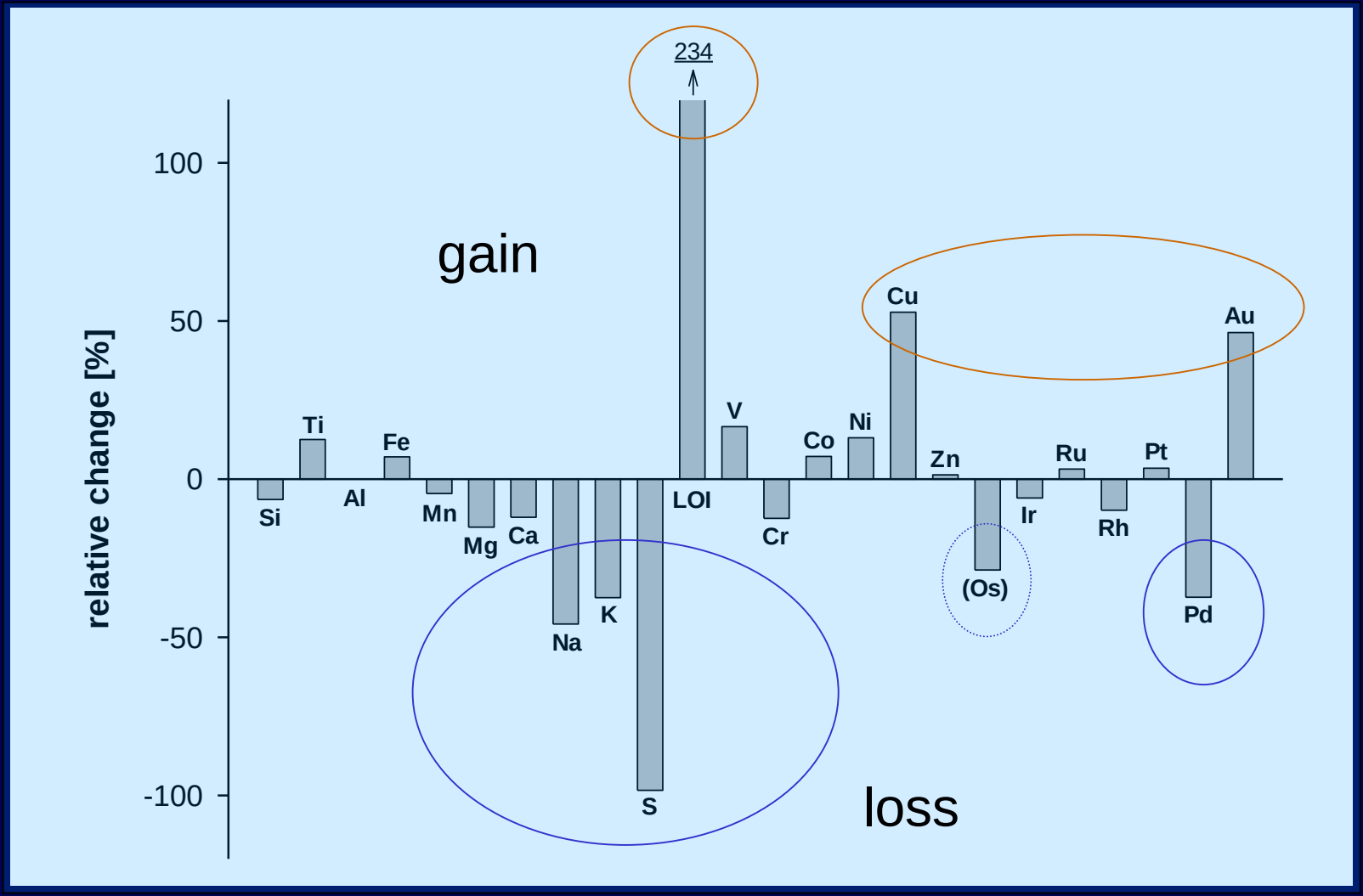
Oxidized MSZ
Hartley Mine (HOP-20x)



Oxidized MSZ
Ngezi (NRC 146)



Geochemical trends: Sulfide ores → oxide ores



MSZ: gains/losses during weathering

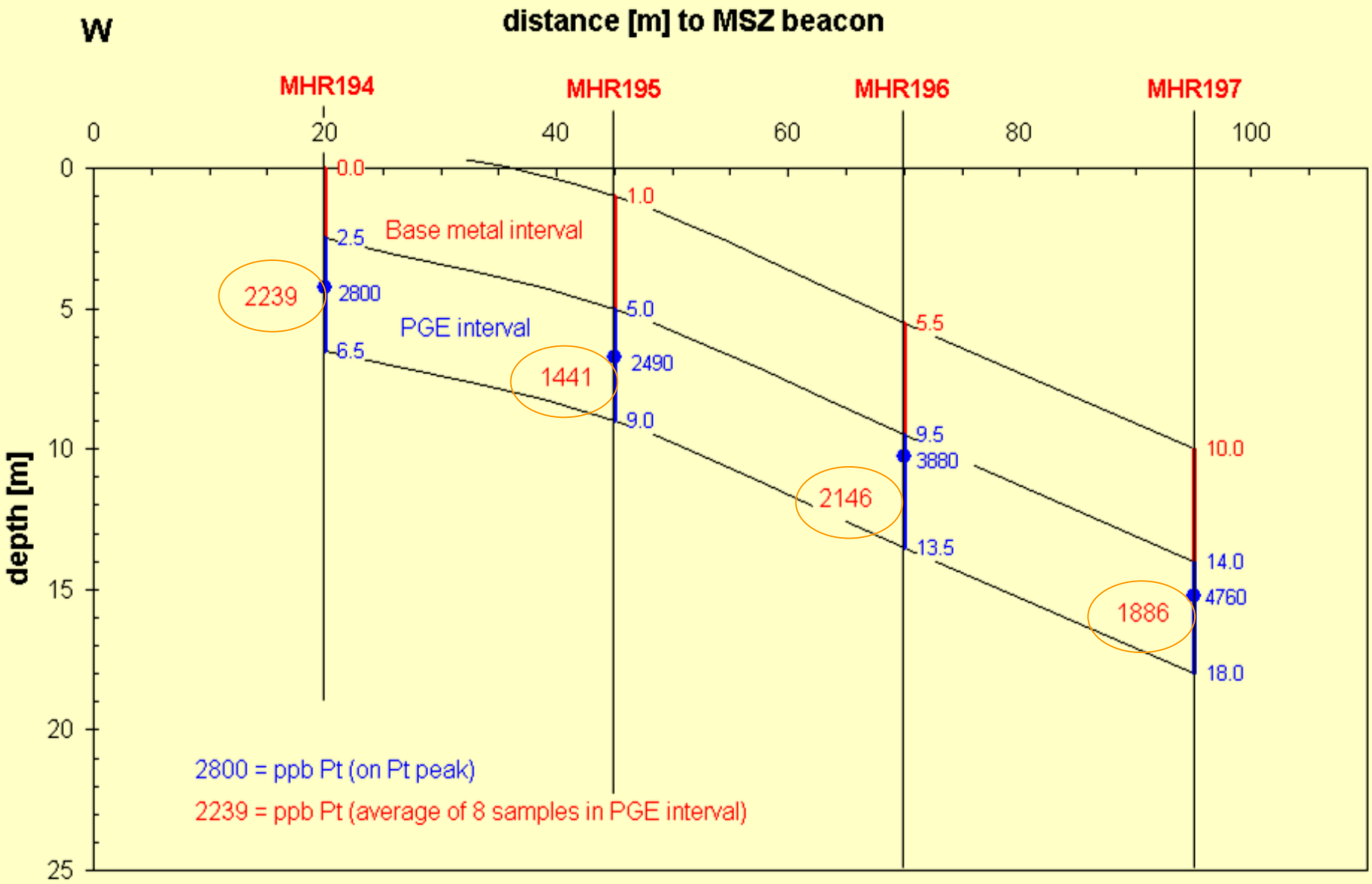
HOP-20x vs. CD-02+SD-04

After Gresens (1967). Al = constant

Oxide Ores

- Geology
- Geochemistry
- Mineralogy

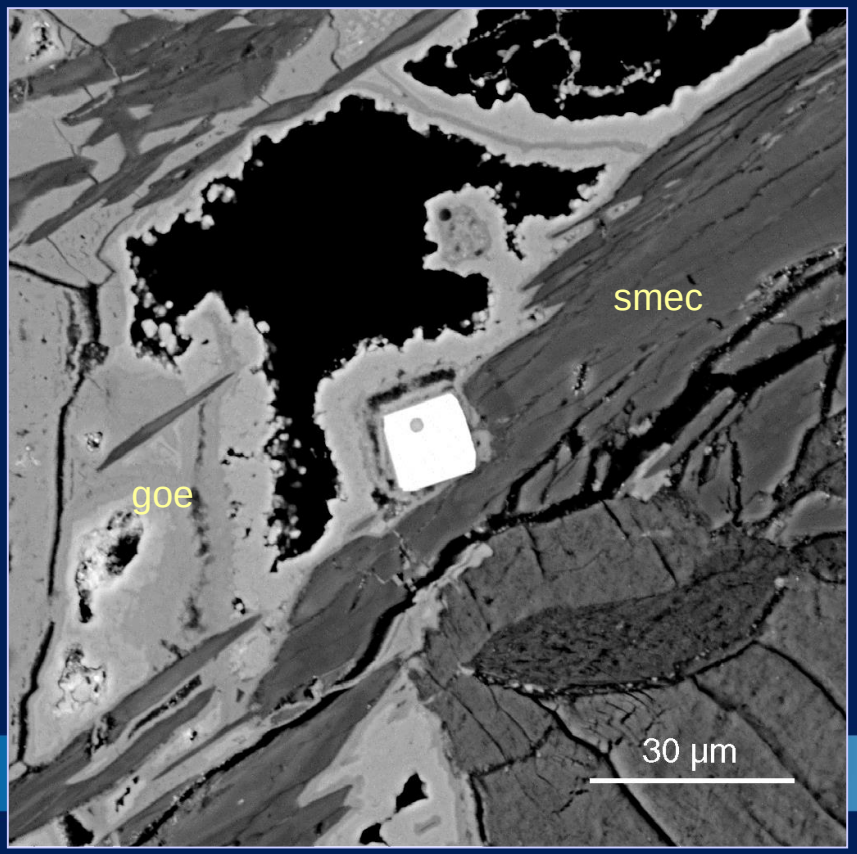
NGEZI (Tiefenprofil)

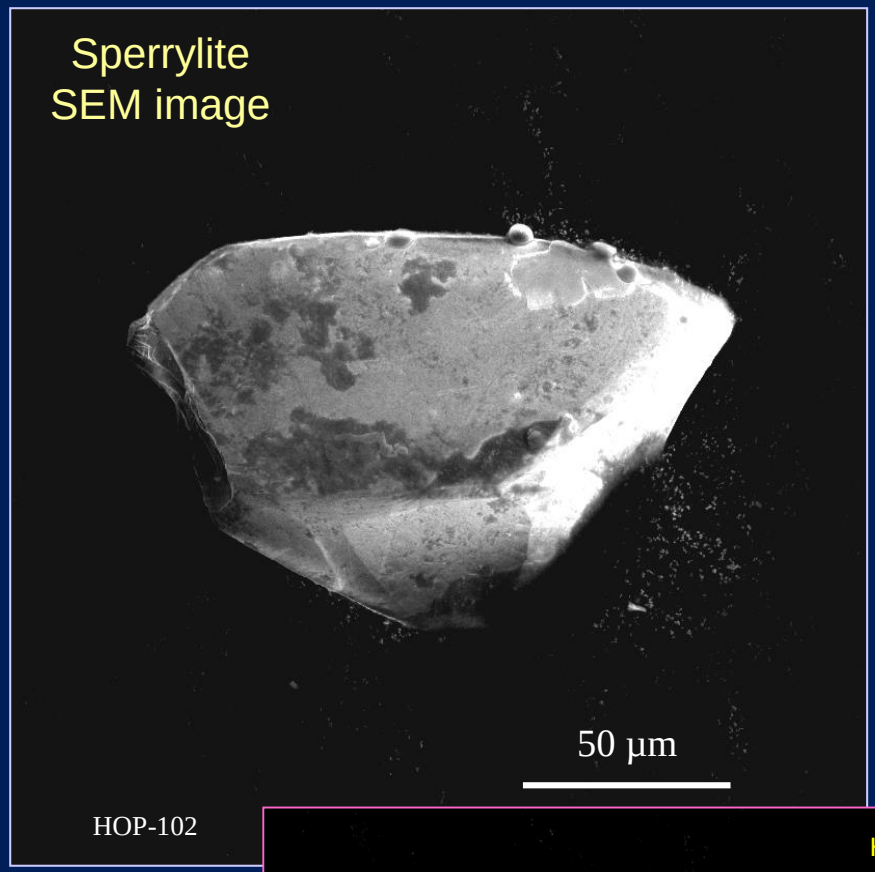


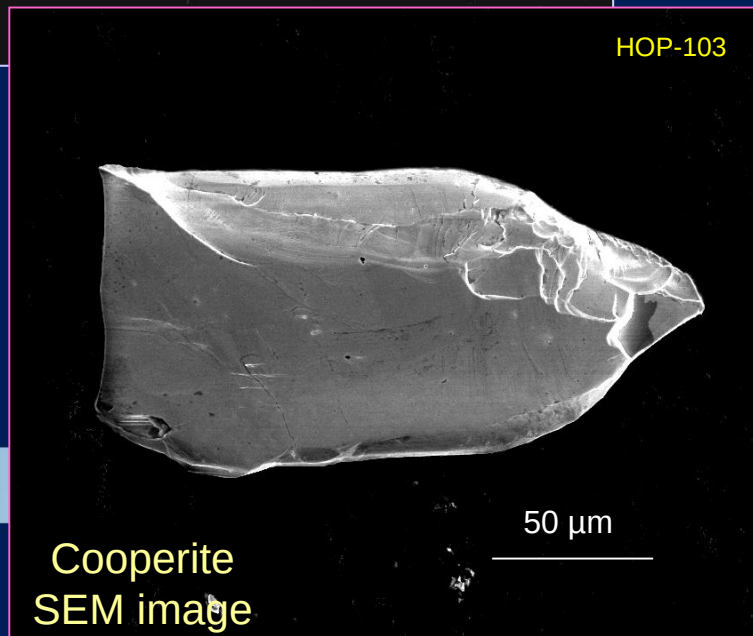
Sample	Depth metres	Degree of oxidation	$PtAs_2$	(Pt,Pd) S	Pt-Fe alloys	(Pt,Pd) (Bi,Te)	Σ PGM	Oxide minerals	Sulfides
MHR 194	4-4.5		1	1	-	-	2	Goethite, chromite	None
MHR 195	6.5-7		-	-	5	-	5	Goethite, hematite, magnetite, chromite	None
MHR 196	10-10.5		9	-	1	1	11	Goethite, hematite, magnetite, rutile	Sparse relicts in silicates
MHR 197	15-15.5		4	12	-	28	44	Magnetite, chromite	Po, pn, cpy, py. Incipient oxidation at rims

Relict PGM

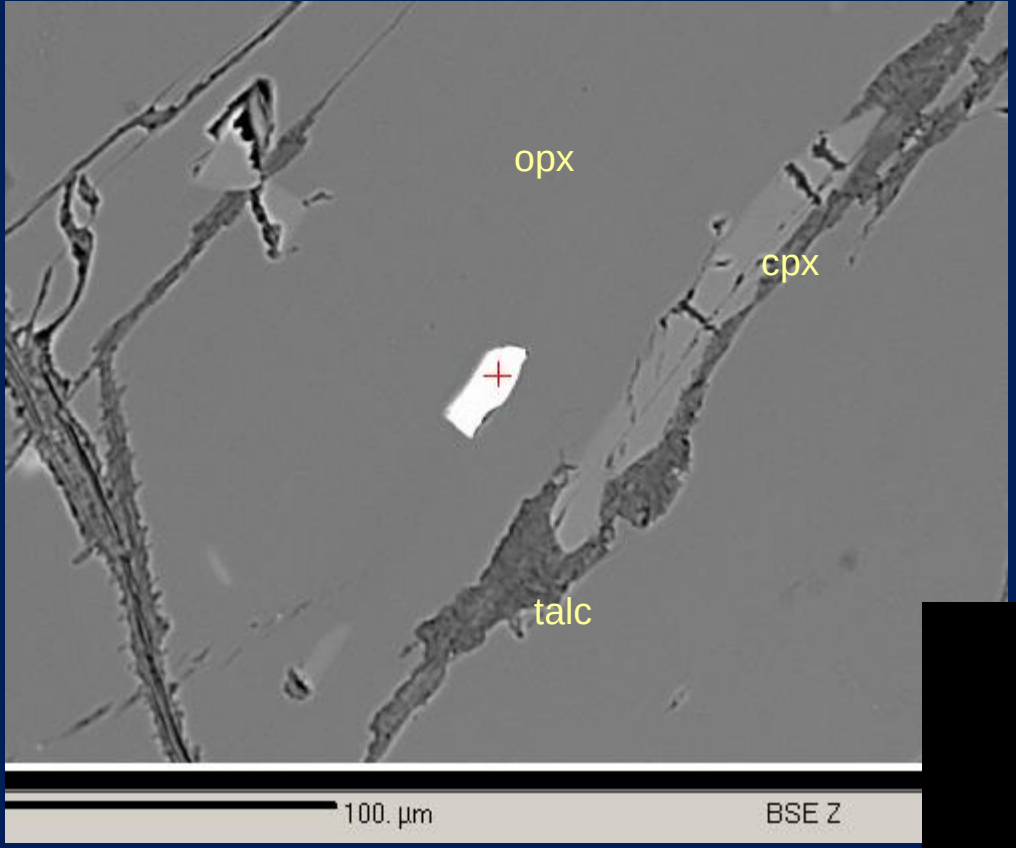
Sperrylite
BSE image
polished section

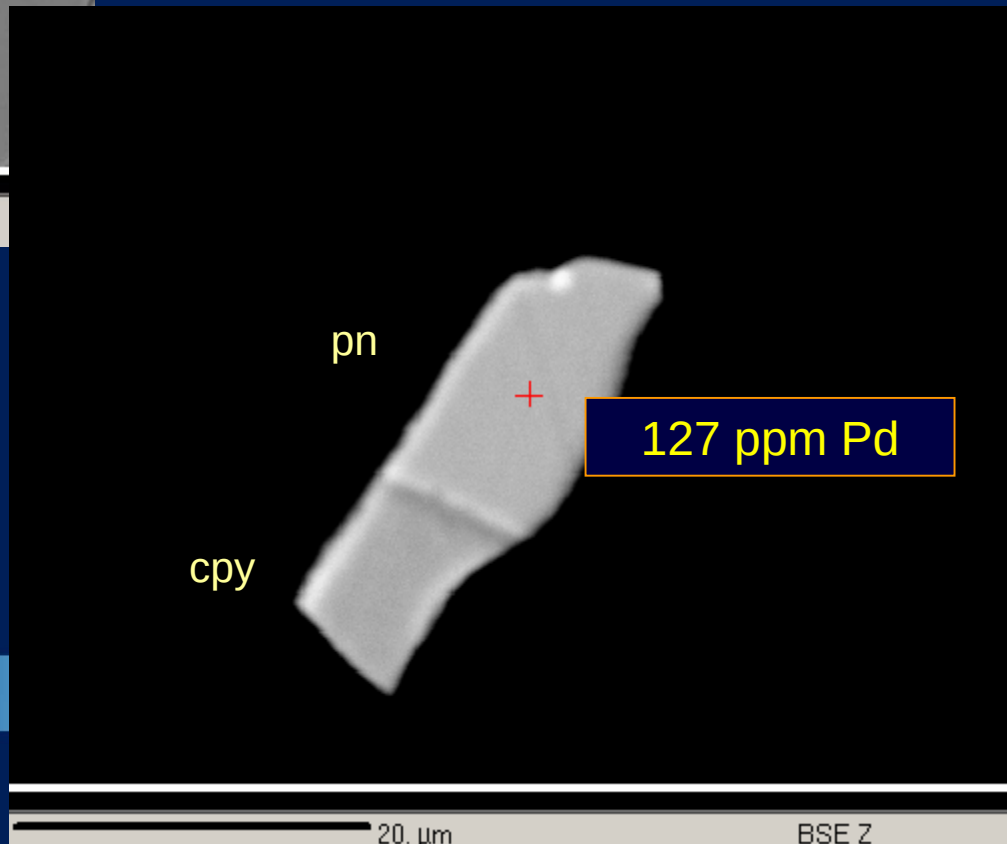






Relict sulfides



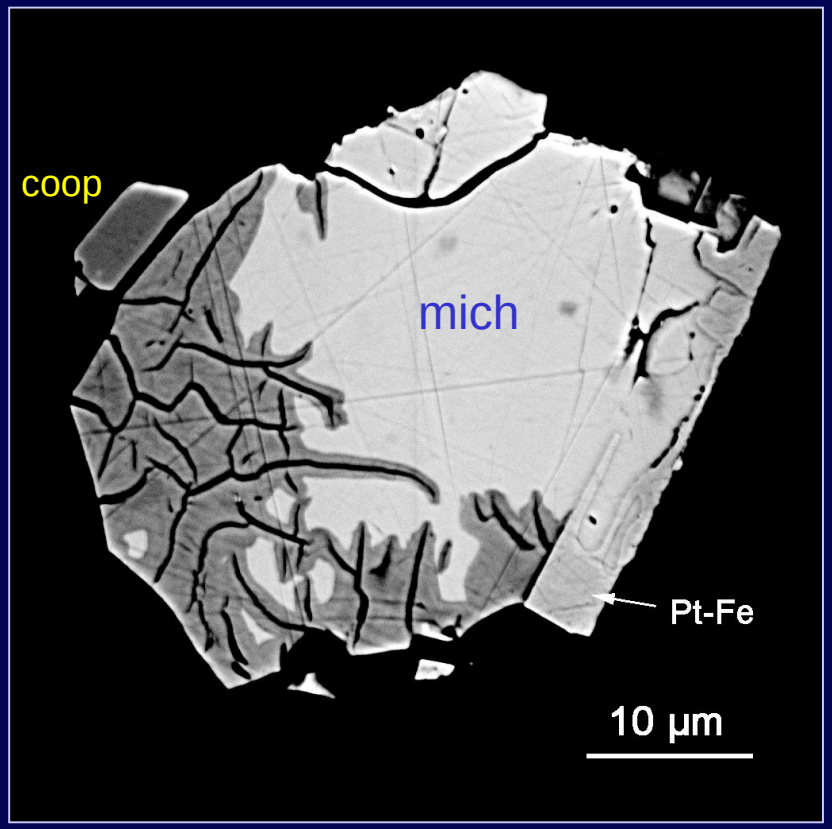


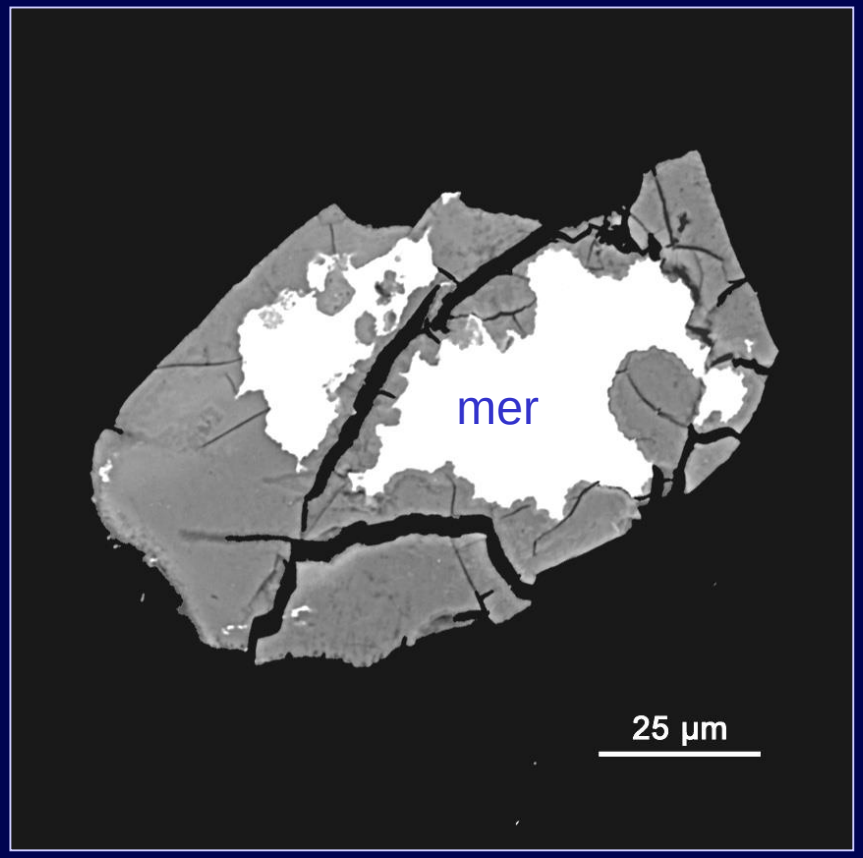
Relict pentlandite:

up to 6500 ppm Pd
up to 450 ppm Pt

HOP-206

Replacements



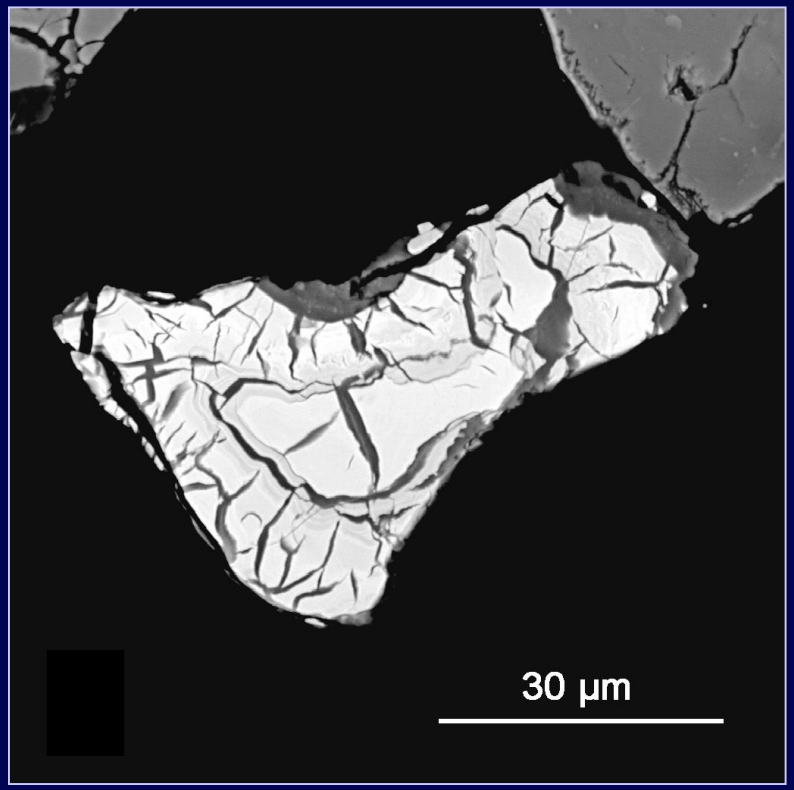


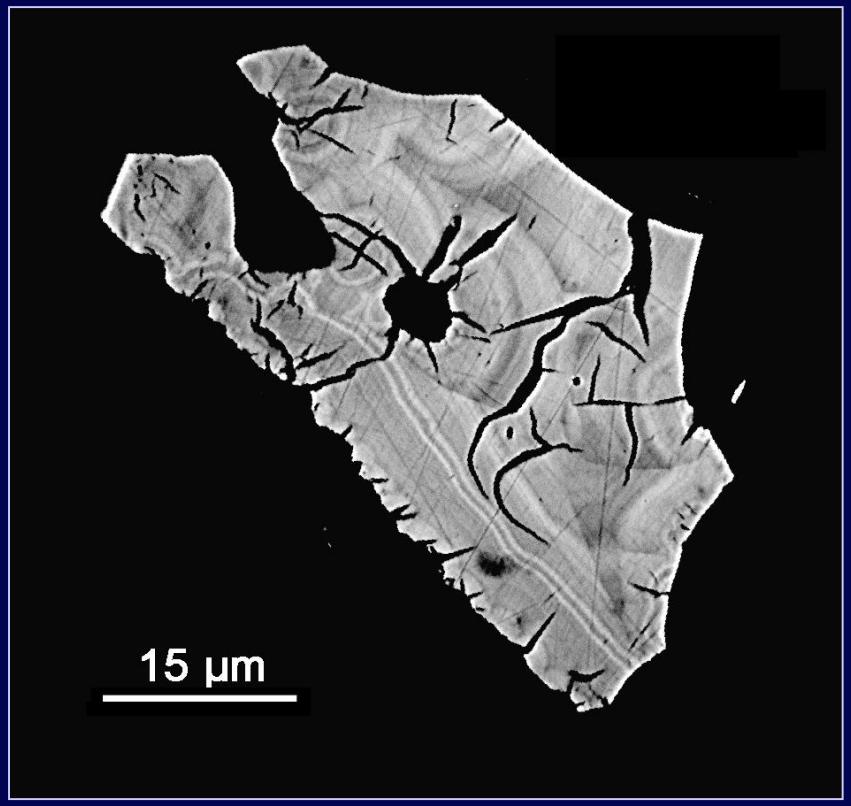
Replacement of (Pt,Pd)(Bi,Te)*

Ngezi Adit A (5711b)

HOP-206 (5910a)

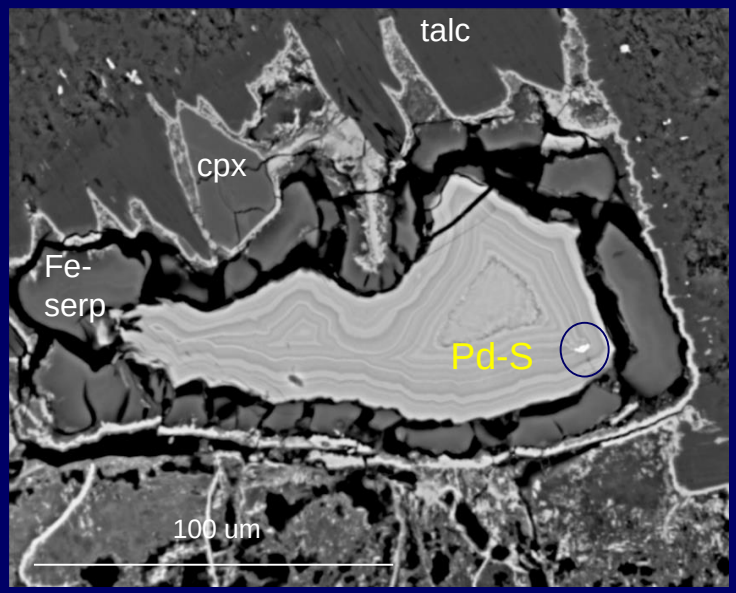
PGE - “Oxides“
Ngezi Mine

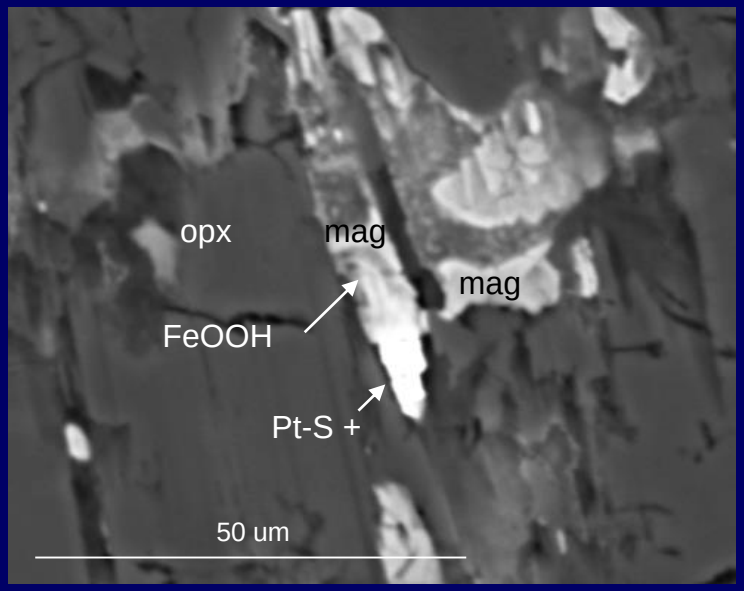




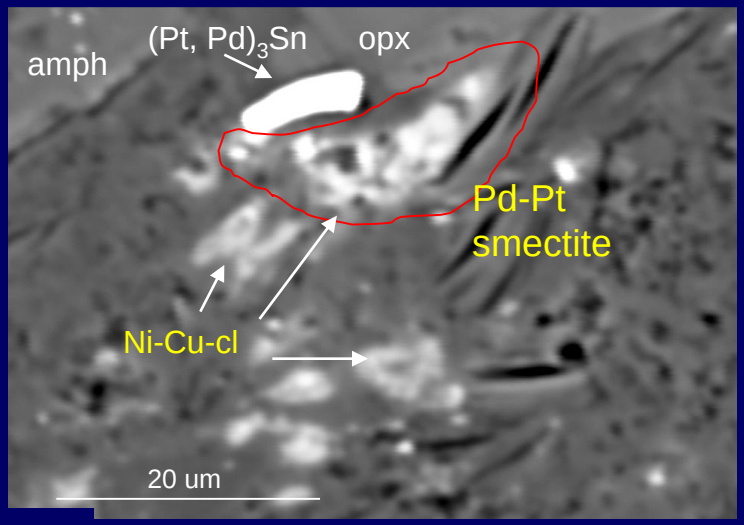
Complete replacements
(or neoformations ?)

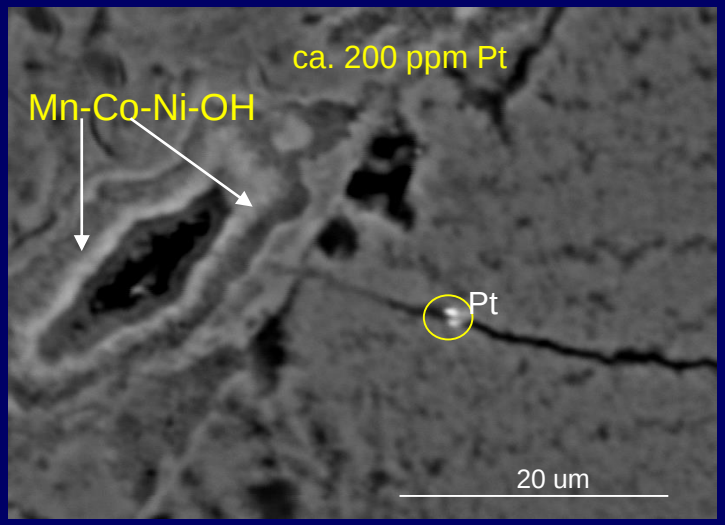
Ngezi Adit A (both 5711b)





PGE in FeOOH, Mn-Co-OH, smectites

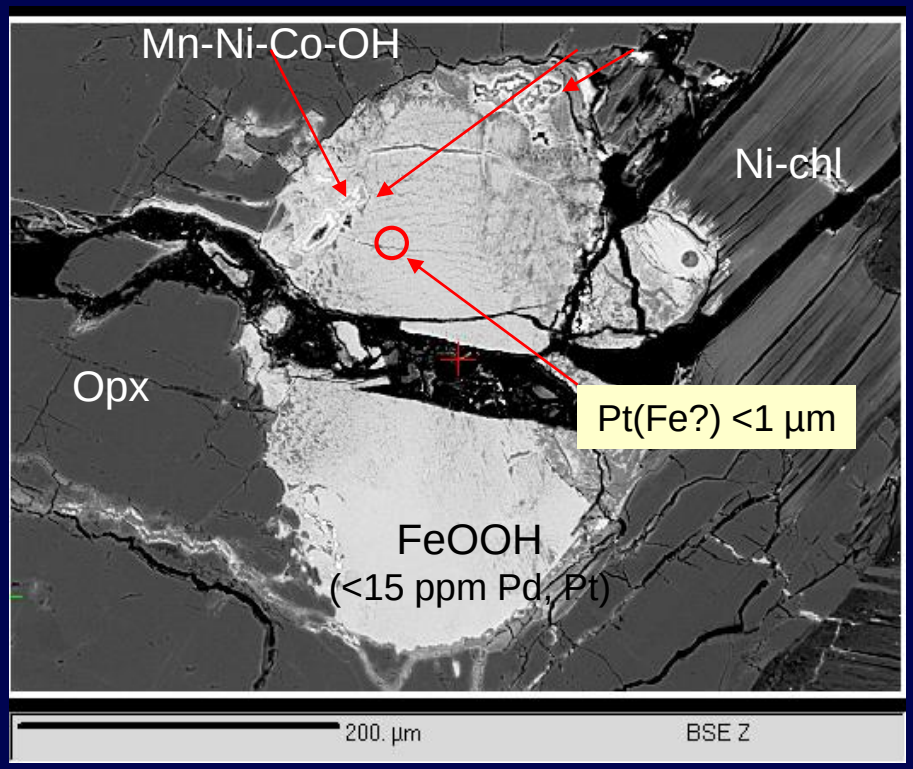


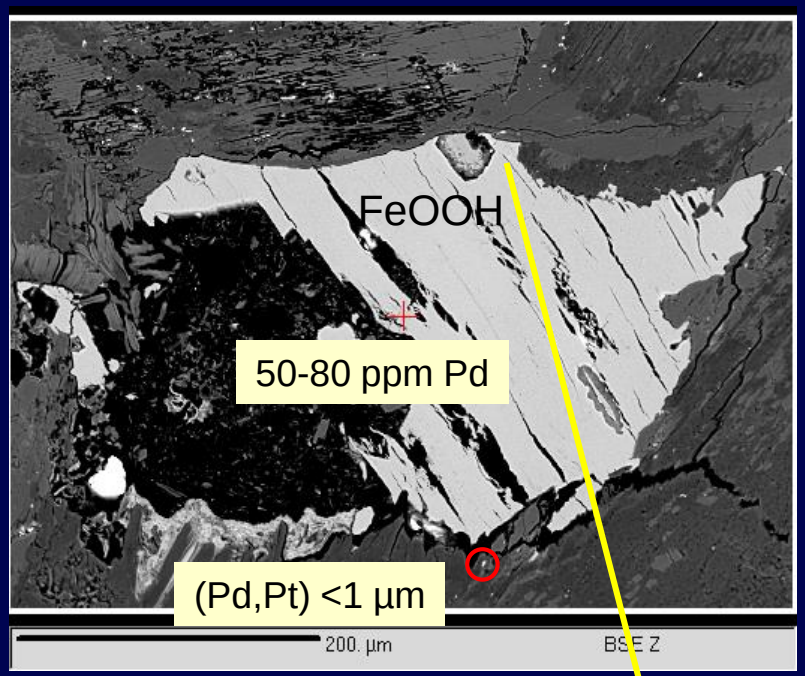


Mimosa

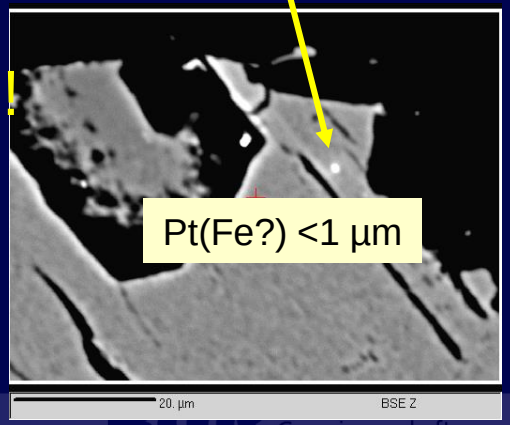
Mimosa

Mn-Ni-Co-OH$_x$ =
200-400 ppm Pt !





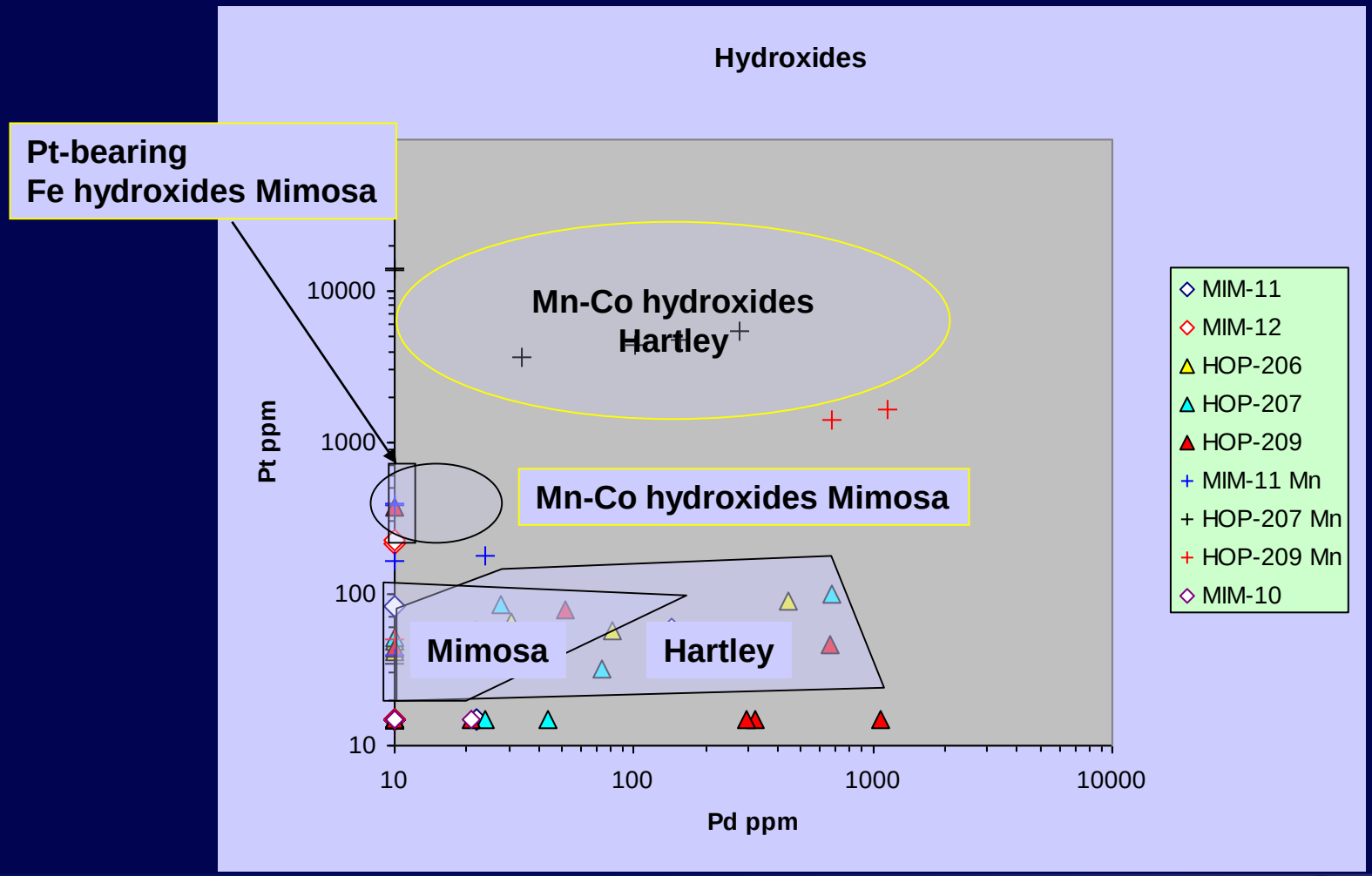
FeOOH =
50-80 ppm Pd !



Pt$_x$-neoformation ?

PGE in FeOOH
and in Mn-Co-OH

Pt and Pd in Mn-Co and Fe-hydroxides



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 ?

Pt distribution

MSZ

sulfide ores	oxidized ores
bimodal	***polymodal***

1) discrete PGM
   $PtAs_2$ & (Pt,Pd,Ni)S
   (Pt,Pd)(Bi,Te)*

> 95%

2) Pt in pn and py

< 5%

~ 25%

PGE - "oxides"
Pt_x (neoformation)
Pt > Pd in FeOOH
Pt > Pd in Mn-Co-OH
Pd > Pt in smectites

~ 75%

Pd distribution

MSZ

sulfide ores	oxidized ores
bimodal	***polymodal***

1) discrete PGM
   (Pd,Pt,Ni)S
   (Pd,Pt)(Bi,Te)*

~20%

2) Pd in pentlandite

~80%

~ 10%

PGE - “oxides“
Pt > Pd in FeOOH
Pt > Pd in Mn-Co-OH
Pd > Pt in smectites

~ 40%

ca. – 50%

PGM / PGE in the exogenic cycle

PGM	MSZ pristine	MSZ oxidized
(Pt,Pd)(Bi,Te)*	30-70%	?
$PtAs_2$	~ 25 %	
(Pt,Pd,Ni)S		
Pd in pentlandite	~ 80% of Pd_{total}	

Metallurgical options for oxide ores

	Method	Recovery
• Grainger Bros. (1926)	Bulk - Gravitation	<< 50% (?)
• Hartley Mine (1997-99)	Bulk - Flotation	30 % (?)
• TML Process BHP – lab scale (1992/1994)	Bulk – Roasting (300-425°C)	
	Br° in NaBr in H_2SO_4	Pt = 85 %
	leach (70°C, 2h)	Rh = 65 %
	CIP	Au = 95 %

problems: costs of chemicals; aggressive acids; environmental issues

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

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

NO

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 lixiviants (Jacobs University Bremen, Germany)

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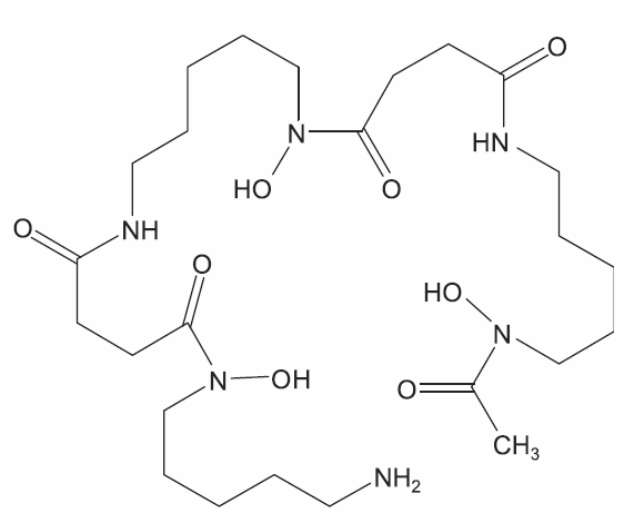
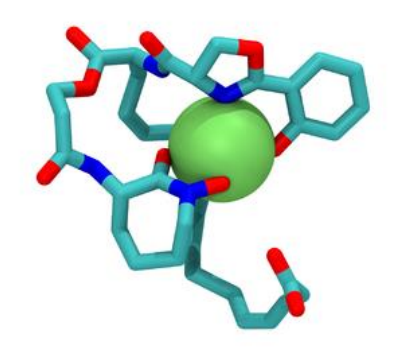
Leaching experiments with siderophores (biologically produced organic ligands)

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



Structure of desferrioxamine B (DFO-B)
Yoshida et al. (2004)



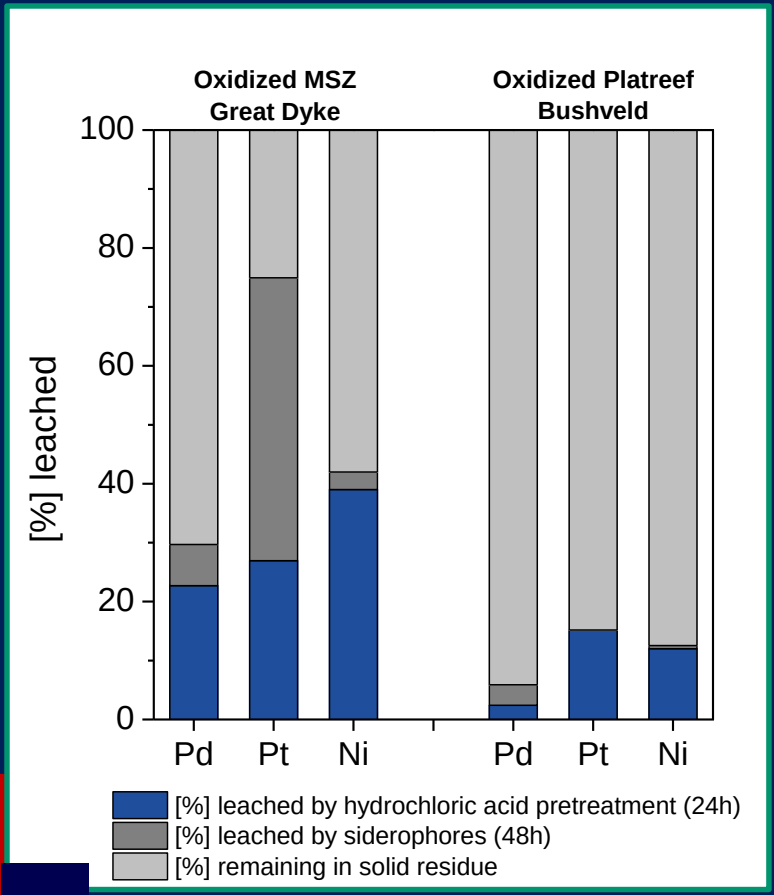
Holmes et al. (2005)

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 !

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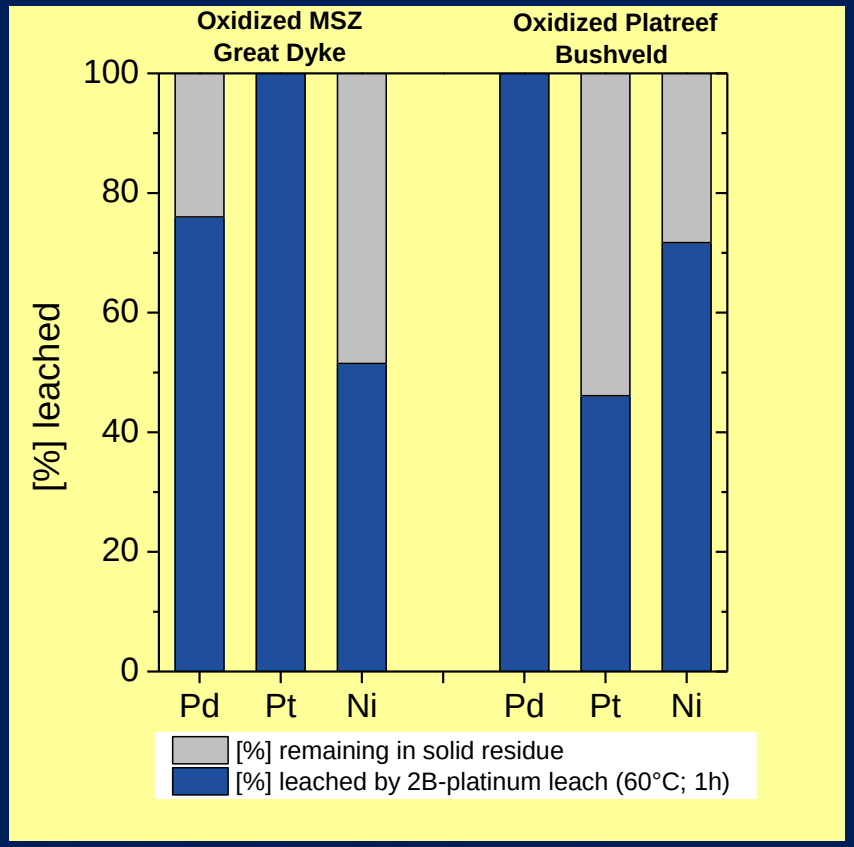
Leaching experiments with inorganic lixiviants

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

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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

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

	Pt [µg/kg]	Pd [µg/kg]	Ni [mg/kg]	Cu [mg/kg]	Cr [mg/kg]
Average (n=6)	1184	924	2050	2088	798

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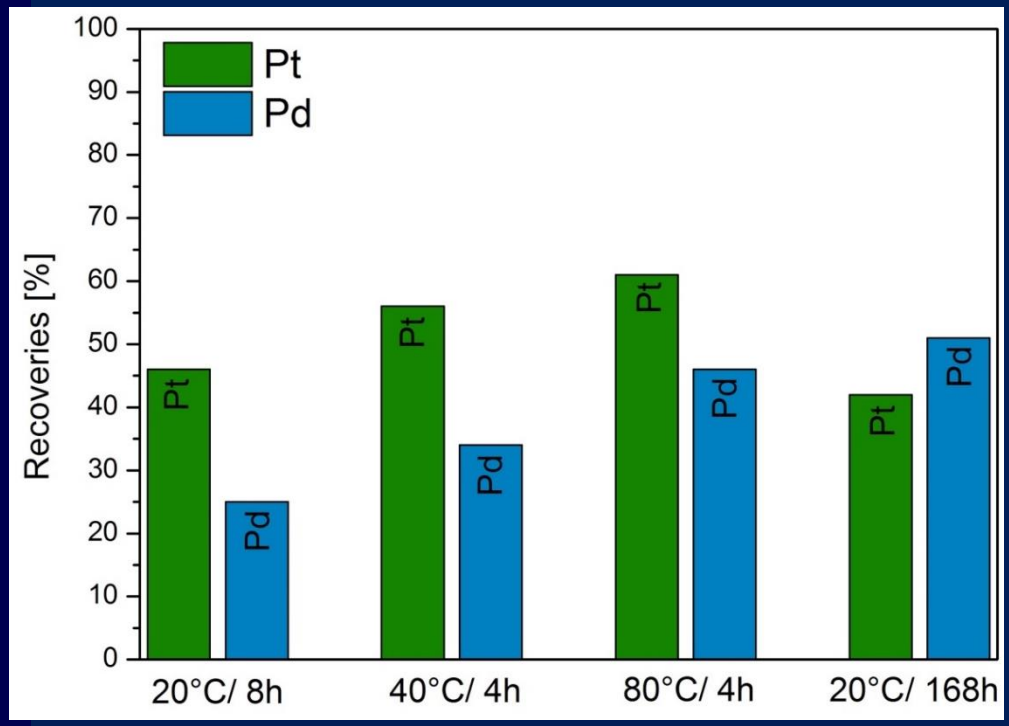
First results – upscaling experiments

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



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Extraction of PGE from oxide ores by hydrometallugical methods

Advantages:

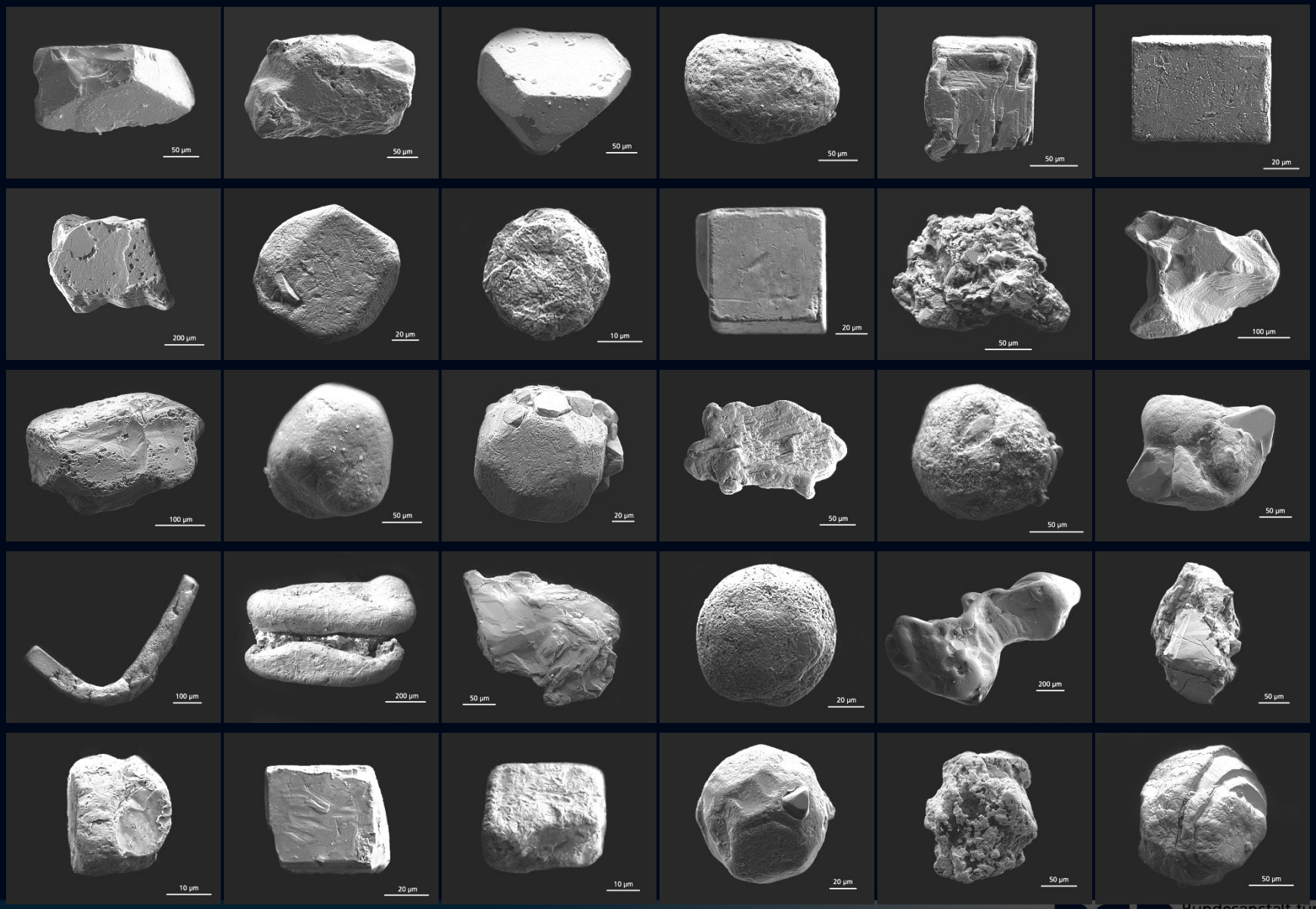
1. Cheap and simple surface mining
2. Pt + Pd are amenable to leaching by various acids
3. Heap-leach/ tank-leach is possible
4. Inexpensive reagents
5. Good/acceptable recoveries
6. Expensive processing steps like fine-milling, flotation, smelting, matte-leaching are not needed

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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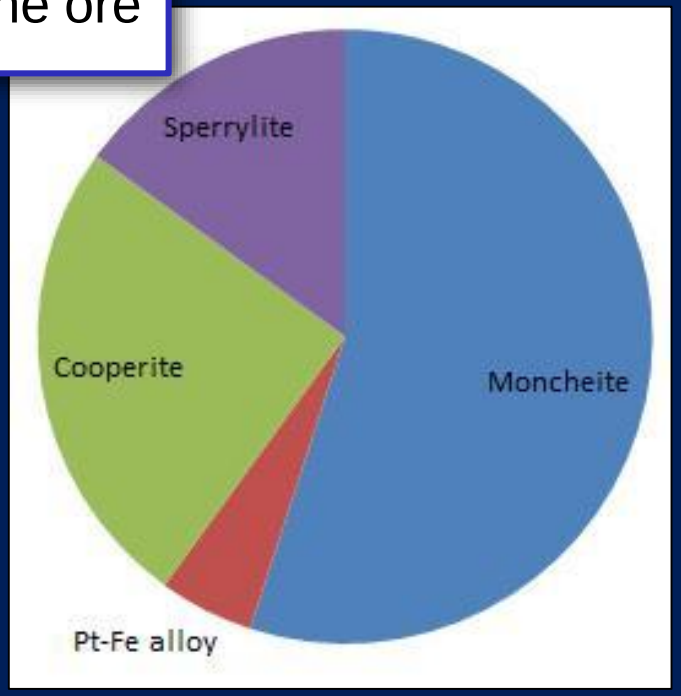
20 µm
50 µm
50 µm

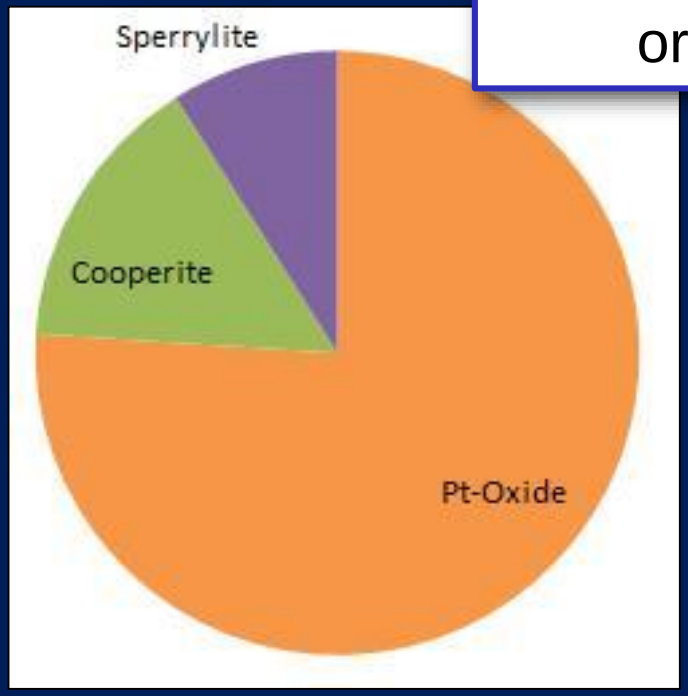
….PGM grains….

weathered PGE ores - MSZ

pristine ore



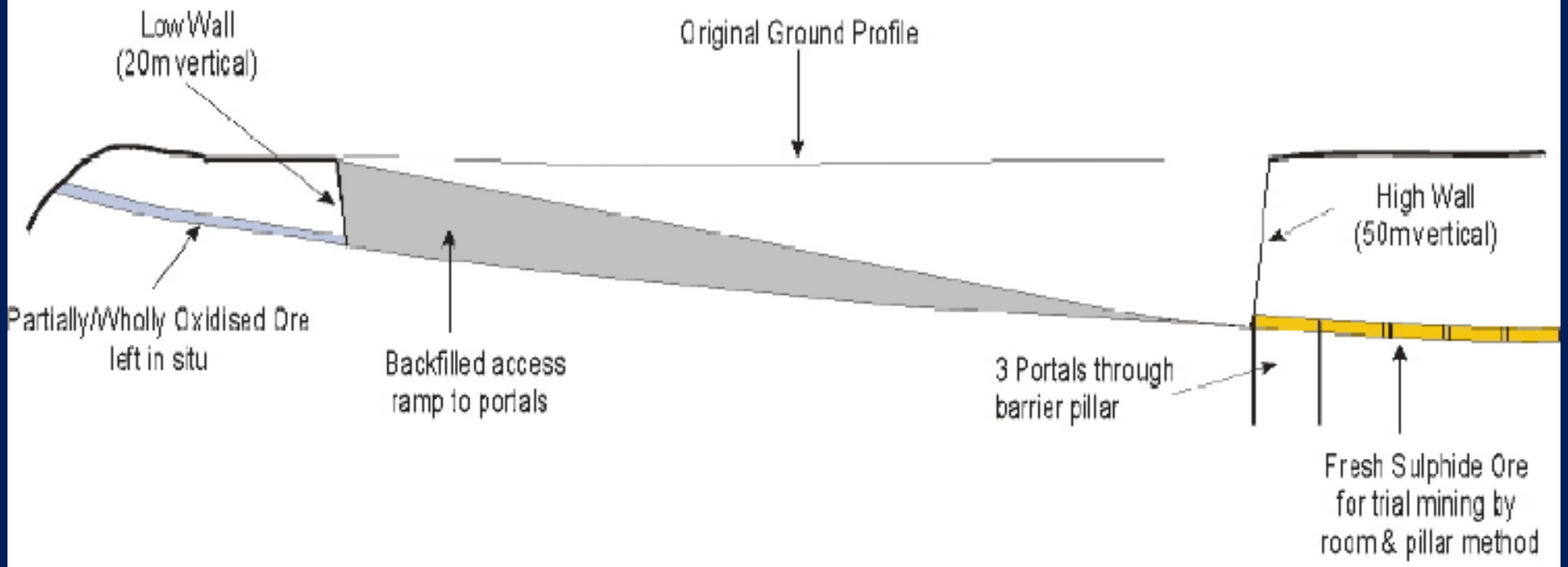
weathered ore



Evans 2000

Ngezi Platinum Mine

E-W section across Trial Mine, looking N



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)

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BGR Bundesanstalt für Geowissenschaften und Rohstoffe

GEOZENTRUM HANNOVER