Isótopos de azufre y oxígeno como trazadores de interacciones entre la atmósfera, suelos, hidrósfera y el yacimiento de sulfuros de la región de Freiberg

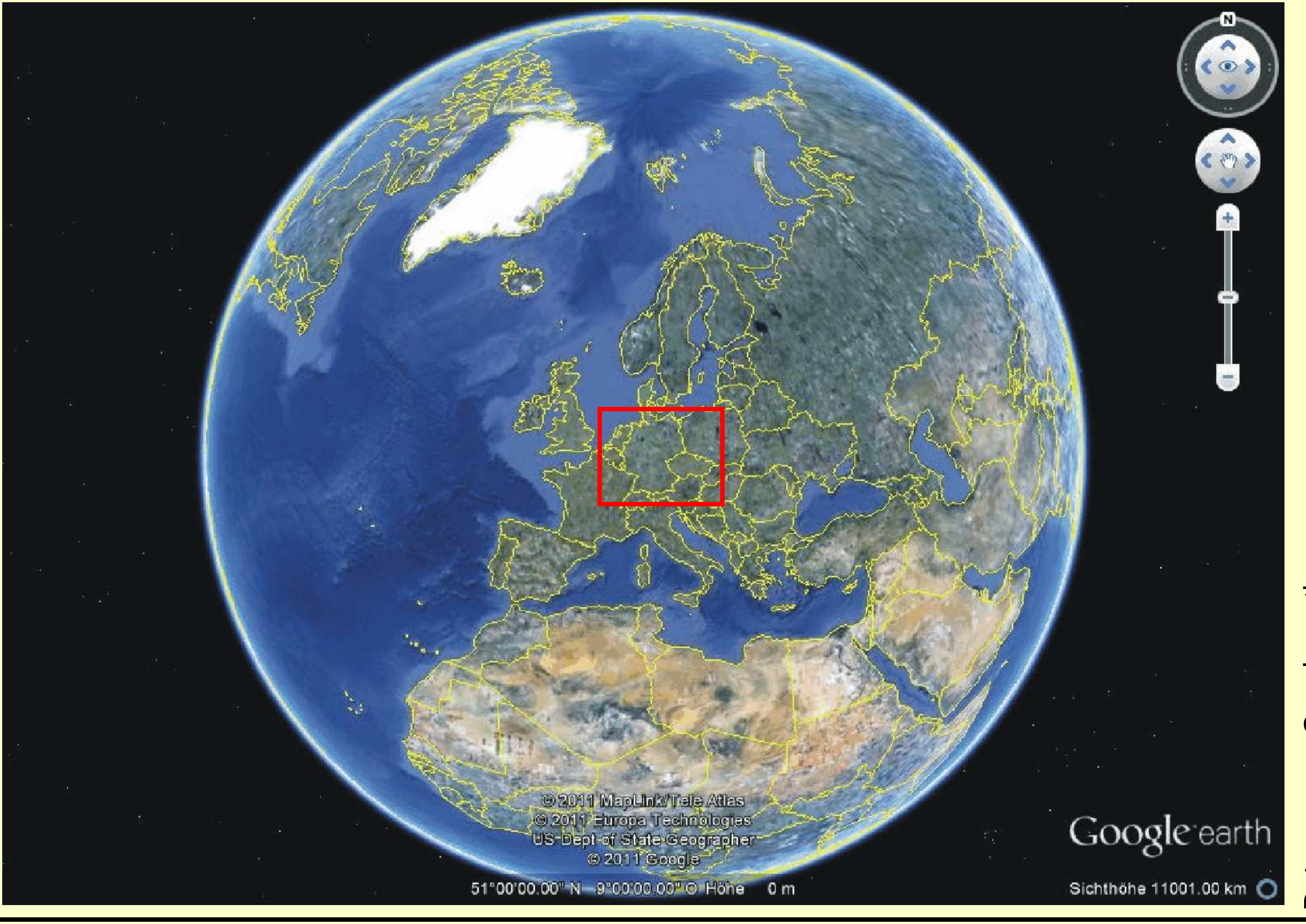
„Schwefel- und Sauerstoffisotope als Tracer für Wechselwirkungen zwischen Atmo-, Pedo-, Hydrosphäre und der Sulfiderzlagerstätte in der Region Freiberg“

Dr. Frank Haubrich, ERZ&STEIN

Content

1. Overview of the region
2. History of mining in the Ore Mountains (Erzgebirge - Montes Metálicos) and consequences for soil contamination (Freiberg)
3. Old mining under the city of Freiberg - oxidation processes of sulphide ores
4. Quantification of heavy metal/As precipitation in the old mine of Freiberg by use of the stable isotopes of sulphur ($\delta^{34}S$) and oxygen ($\delta^{18}O$).
5. Conclusions

1. Overview of the region

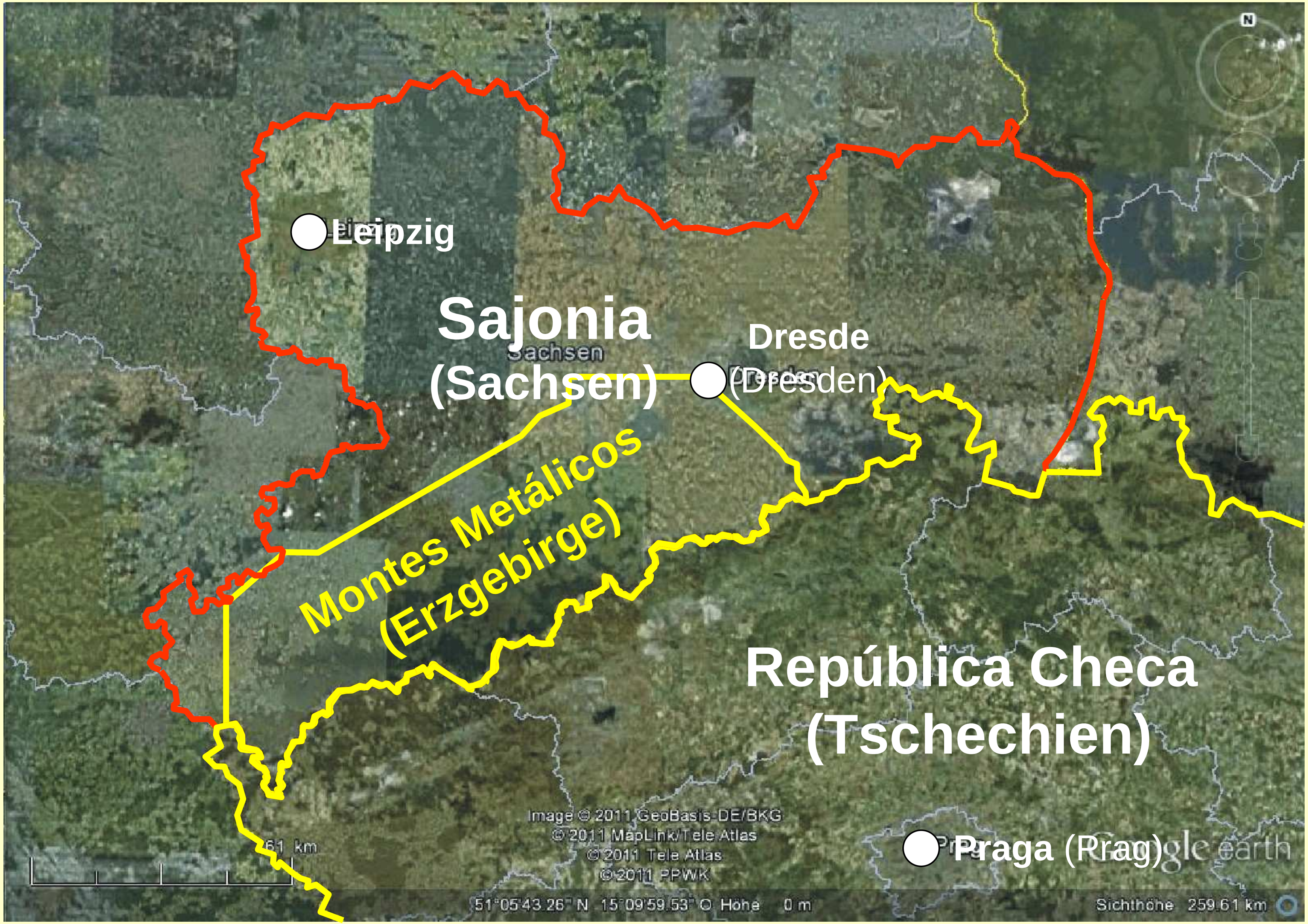


Data source: Google earth

1. Overview of the region

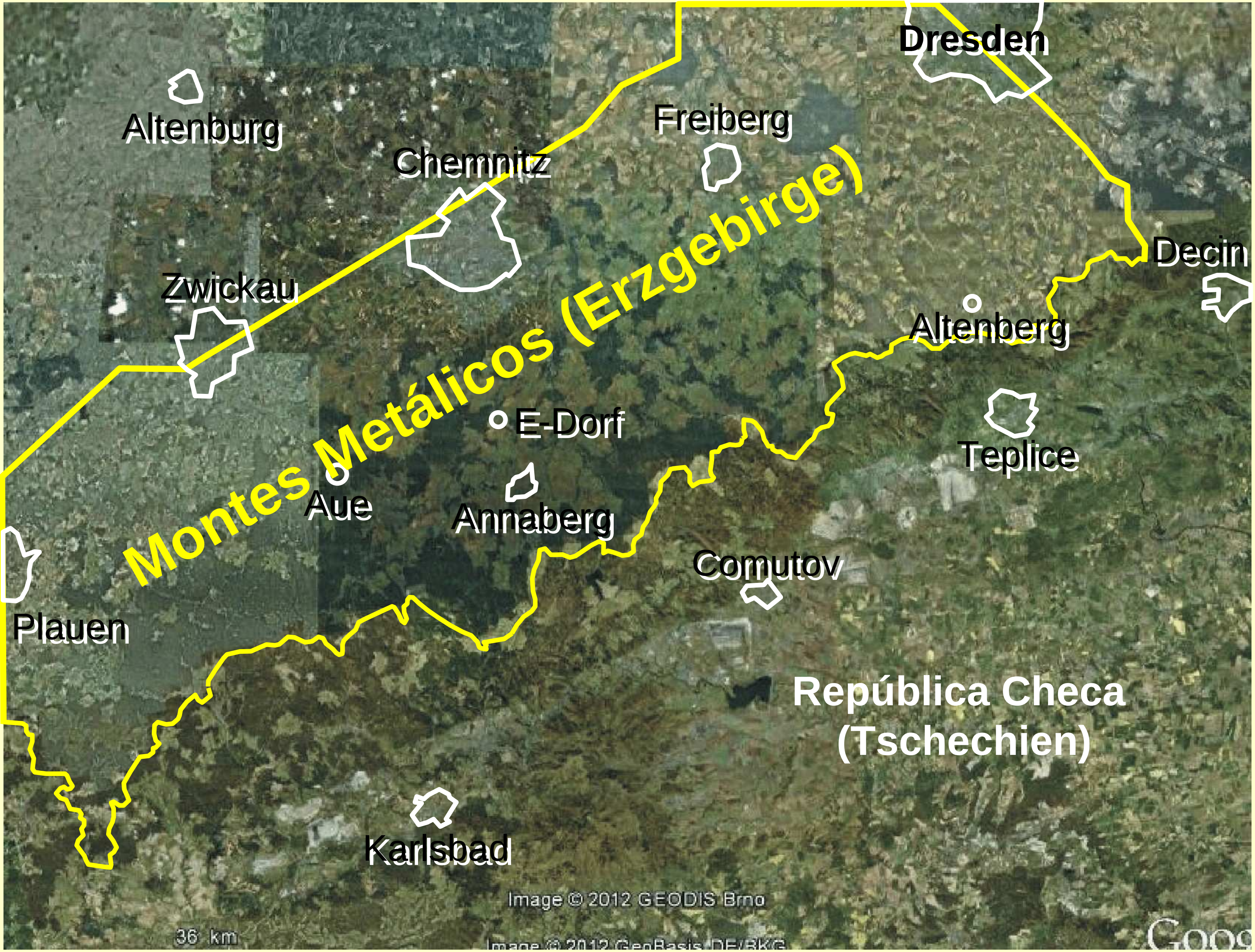
Data source: Google earth

1. Overview of the region



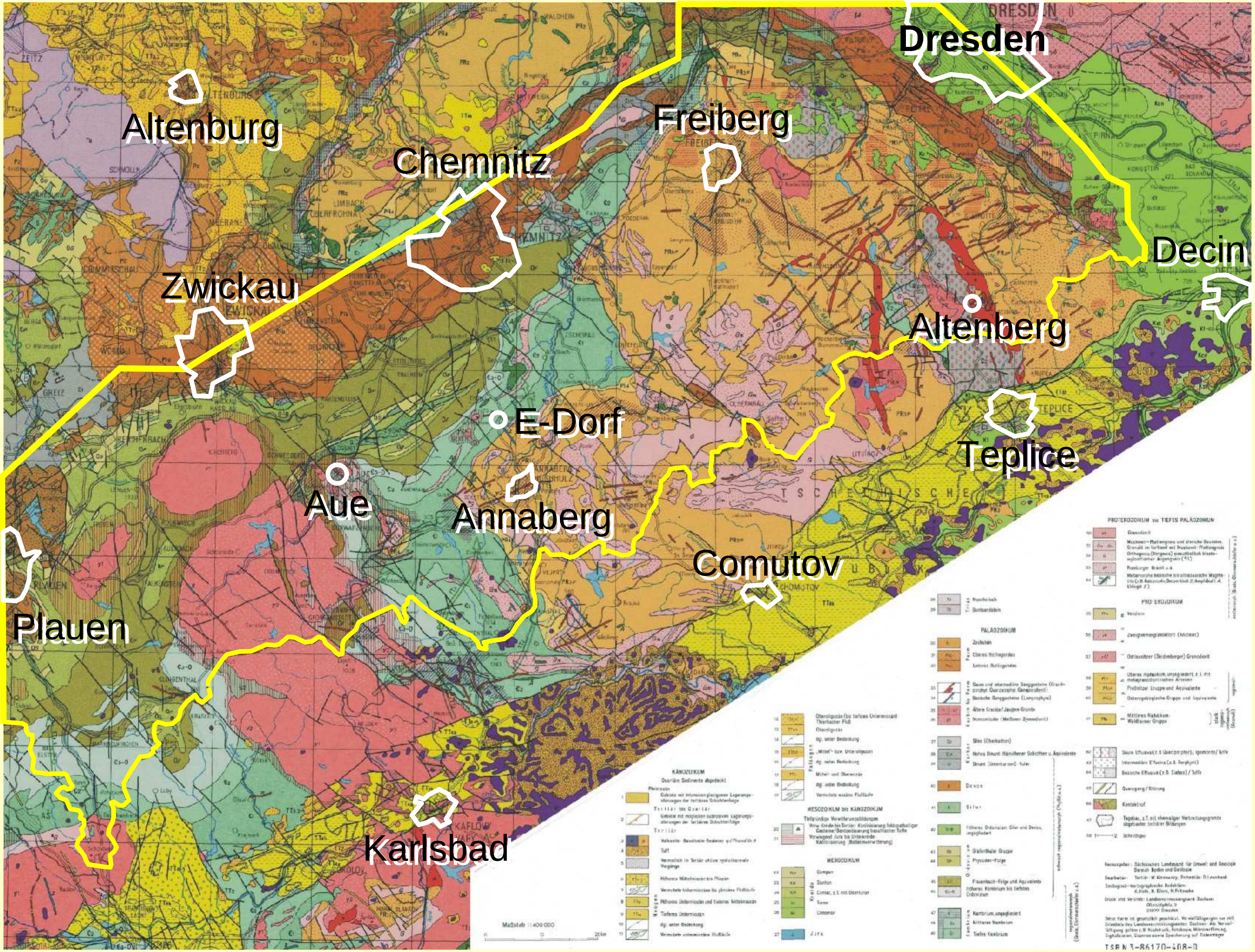
Data source: Google earth

1. Overview of the region



Data source: Google earth

1. Geological overview of the Ore mountains



Data source: Landesamt für Landwirtschaft, Umwelt und Geologie Sachsen

2. History of 800-years mining at the Ore Mountains

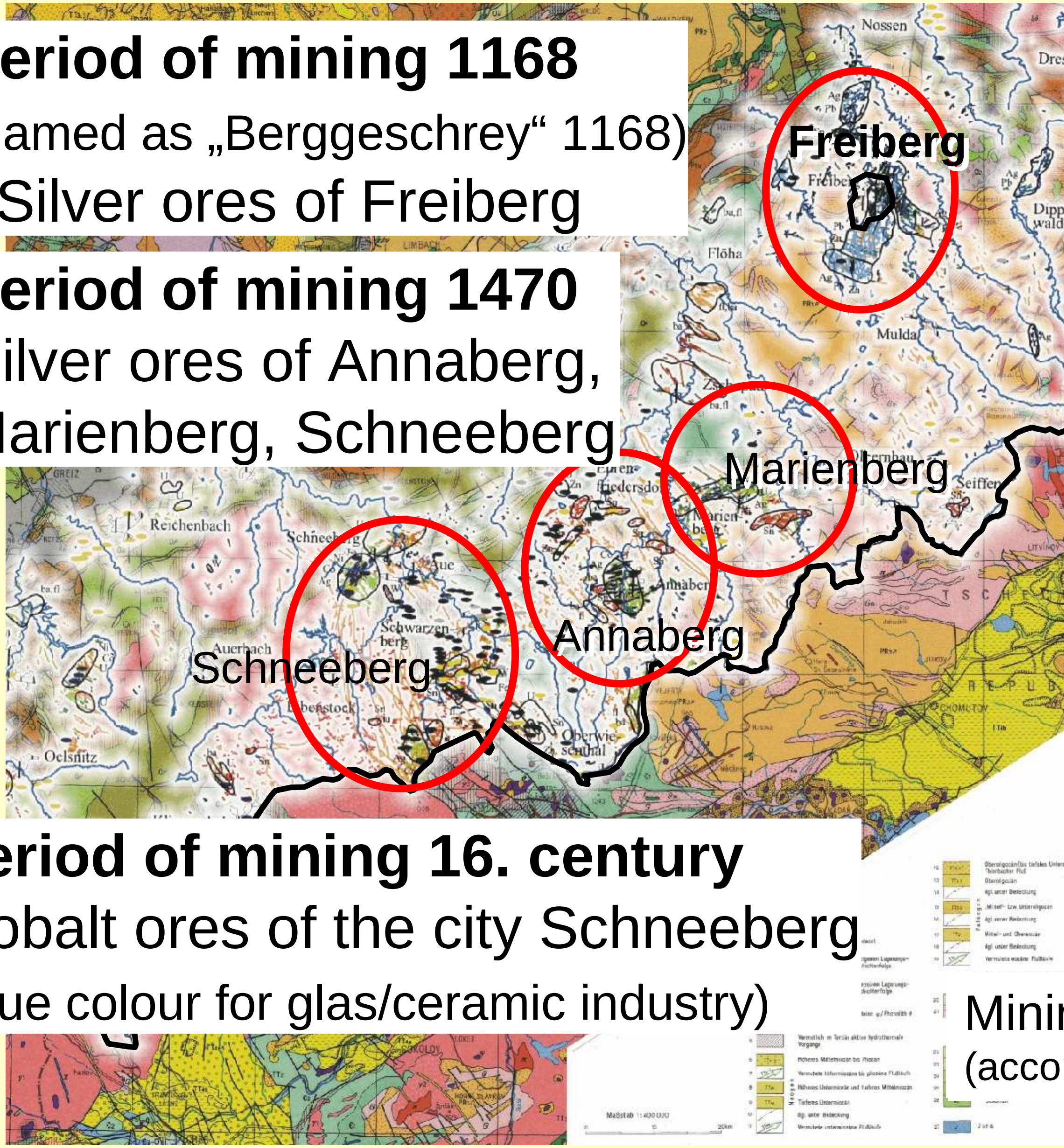
1. Period of mining 1168

(named as „Berggeschrey“ 1168)

- Silver ores of Freiberg

2. Period of mining 1470

- Silver ores of Annaberg, Marienberg, Schneeberg



Period of mining 16. century

- Cobalt ores of the city Schneeberg

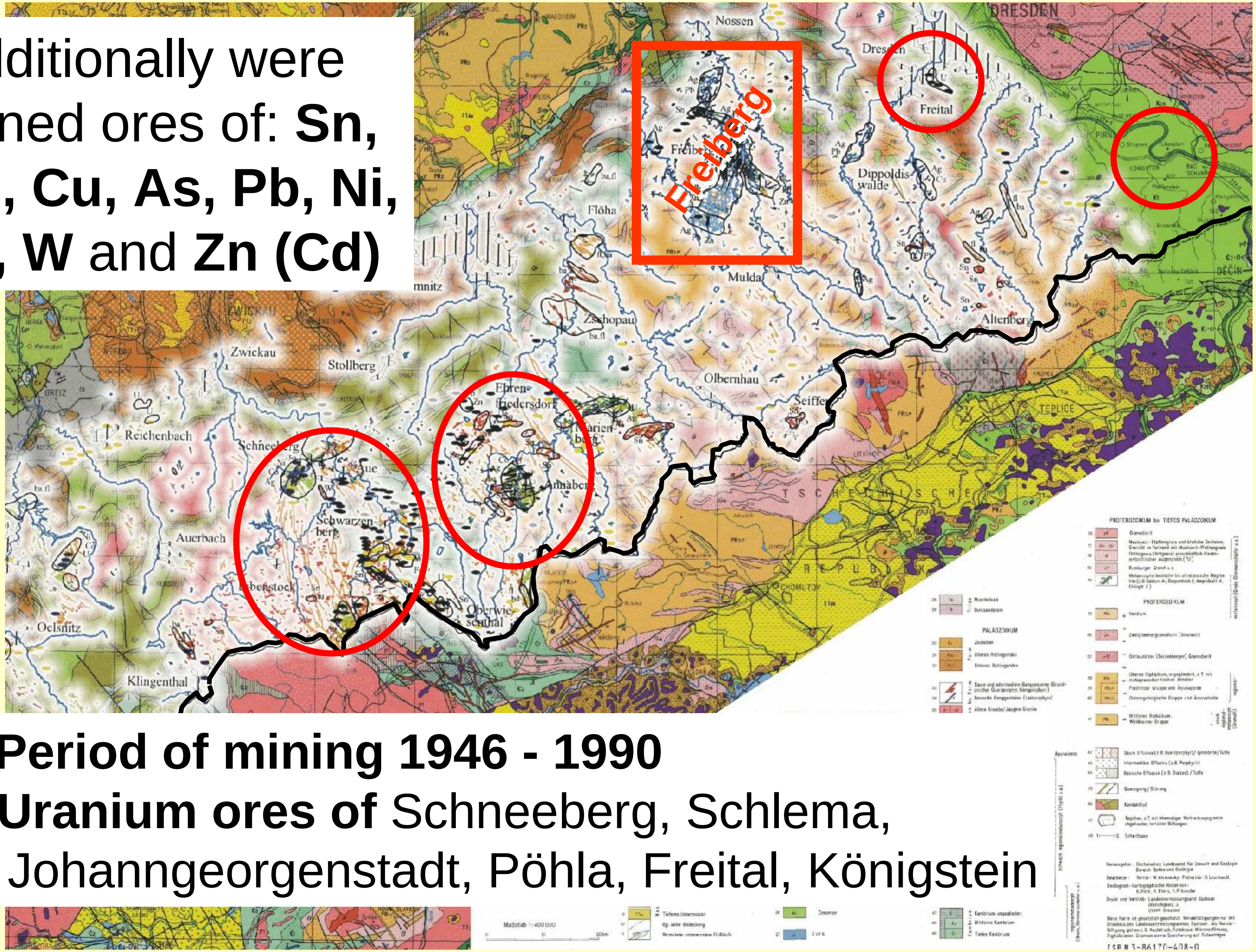
(blue colour for glas/ceramic industry)

Mining with hammer and pick

(accoring Agricola, 1556)

2. History of 800-years mining at the Ore Mountains

Additionally were mined ores of: **Sn, Fe, Cu, As, Pb, Ni, Bi, W** and **Zn (Cd)**

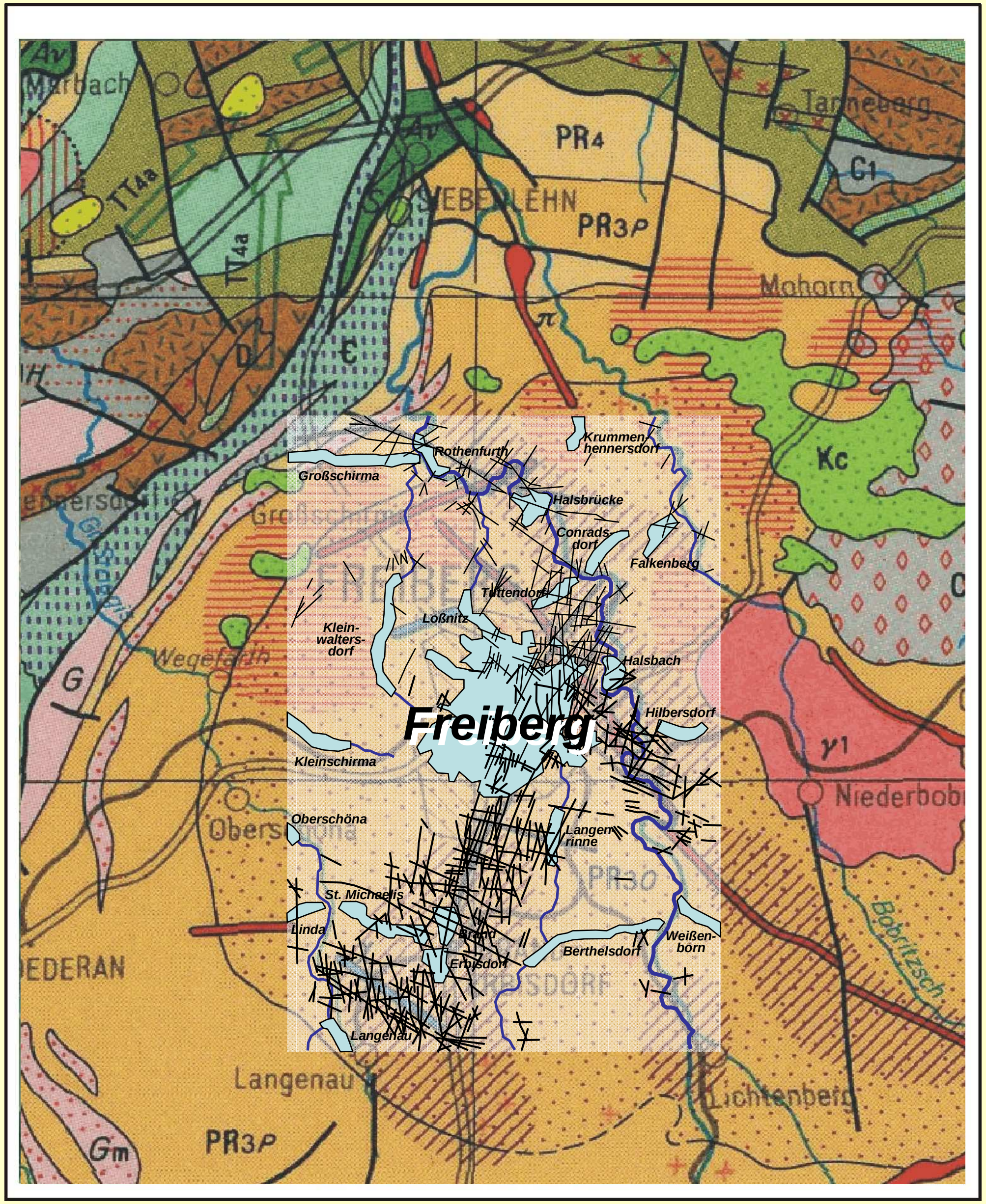


3. Period of mining 1946 - 1990

- **Uranium ores of** Schneeberg, Schlema, Johanngeorgenstadt, Pöhla, Freital, Königstein

Data source: Landesamt für Landwirtschaft, Umwelt und Geologie Sachsen

2. Geology and ore lodes in the Freiberg district



Polymetallic sulfide deposit

More than 1000 ore lodes with:

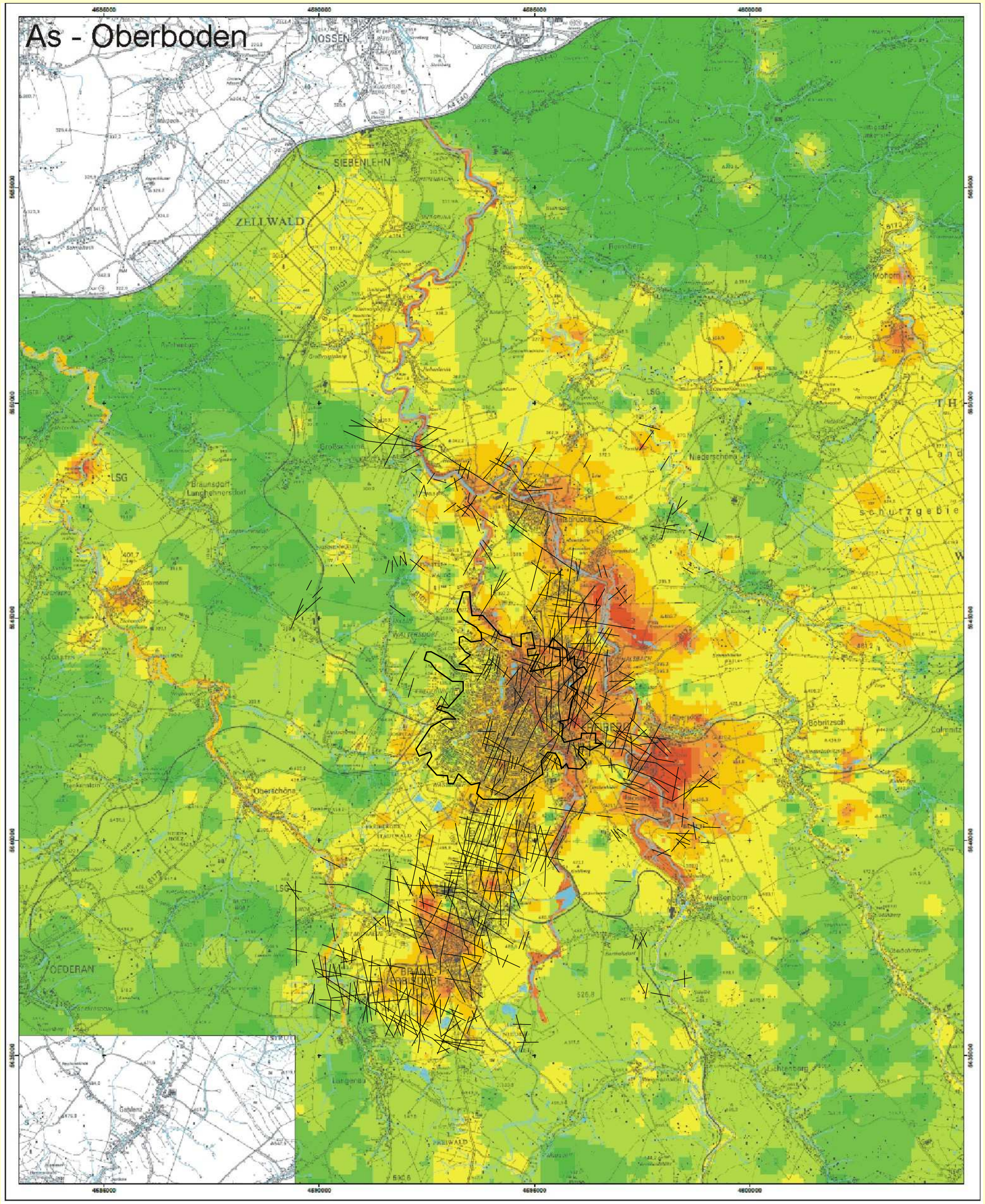
Galenite (PbS with 0,1-0,3% Ag)
Sphalerite (ZnS with Cd)
Pyrite (FeS_2)
Arsenopyrite (FeAsS)
Chalcopyrite ($CuFeS_2$)
native silver (Ag)
div. Ag-ores (Argentite, Proustite, …)
Fluorite (CaF_2)
Baryte ($BaSO_4$)

In Freiberg production of:

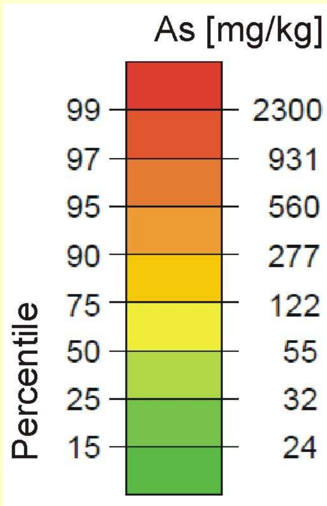
- Ag up to the 19th century
- Pb, Zn in the 20th century

Data source: Landesamt für Landwirtschaft, Umwelt und Geologie Sachsen

2. As in top soils

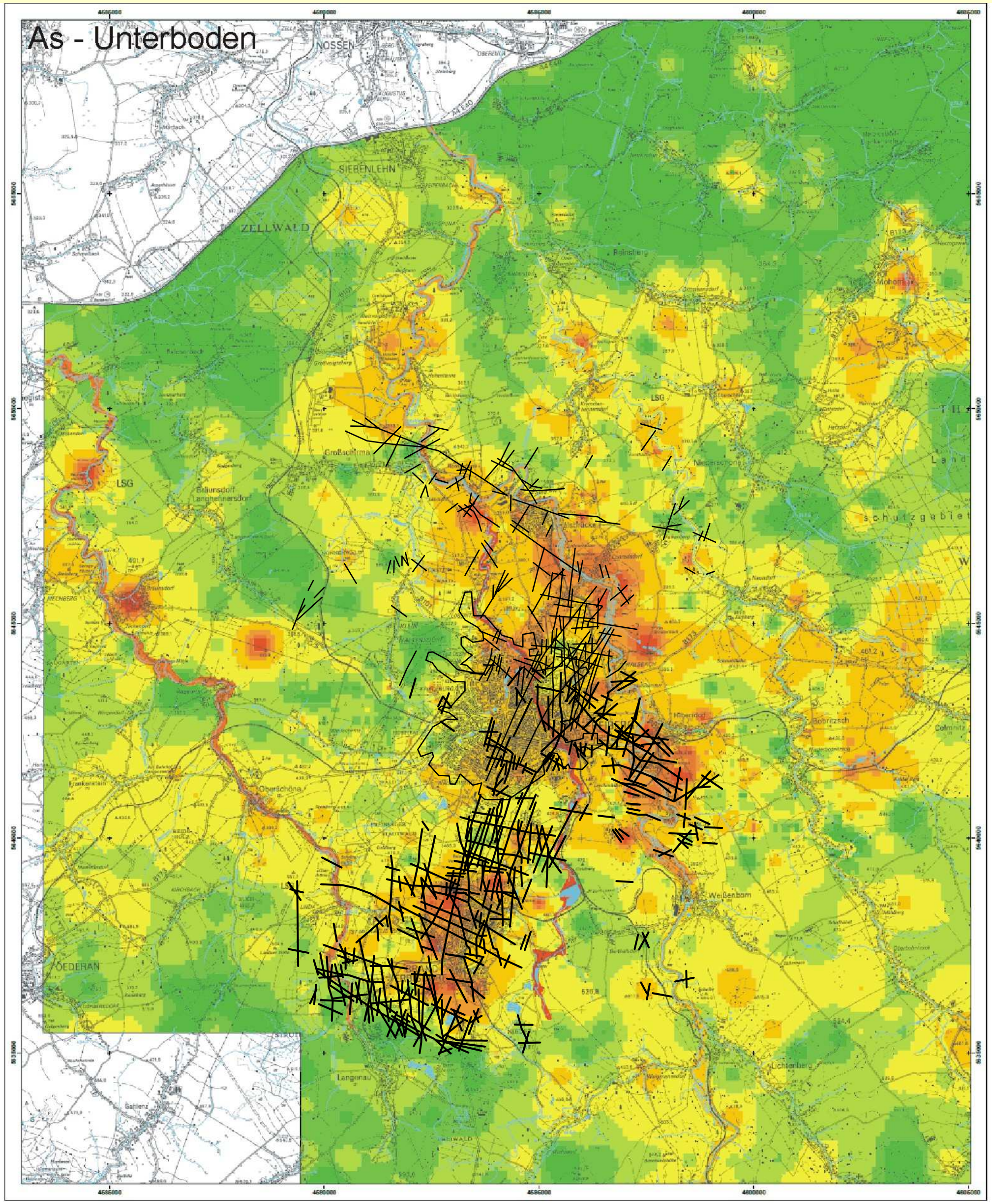


Data source:
Landesamt für Landwirtschaft, Umwelt und Geologie Sachsen (G. Rank, K. Kardel)

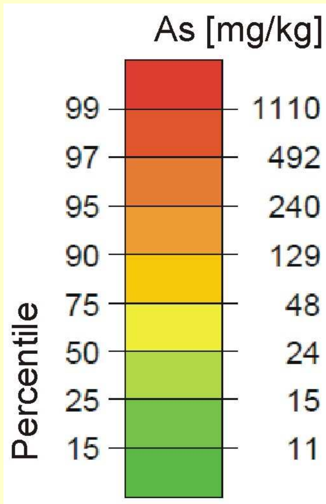


(total content)

2. As in sub soils

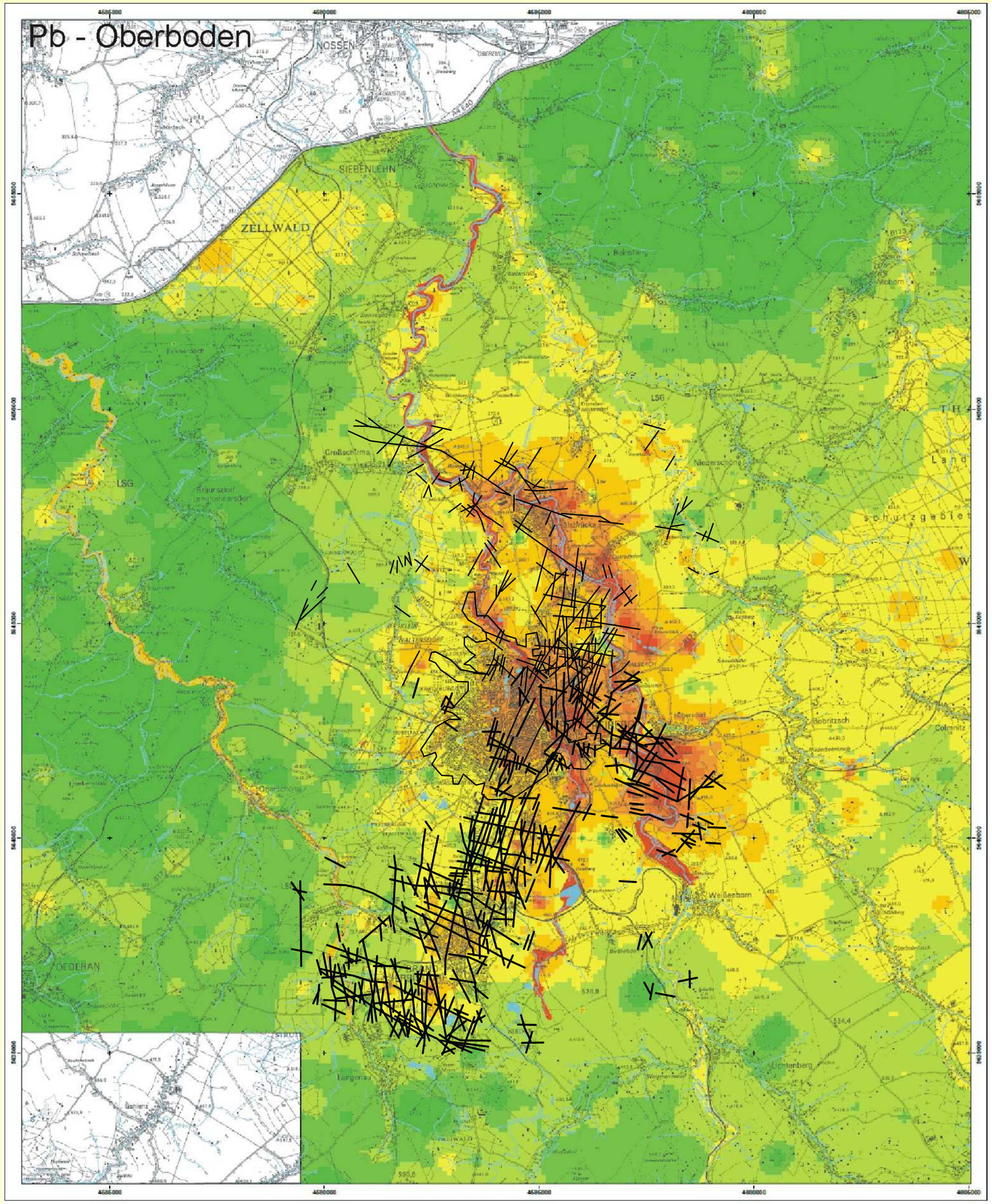


Data source:
Landesamt für Landwirtschaft, Umwelt und Geologie Sachsen (G. Rank, K. Kardel)

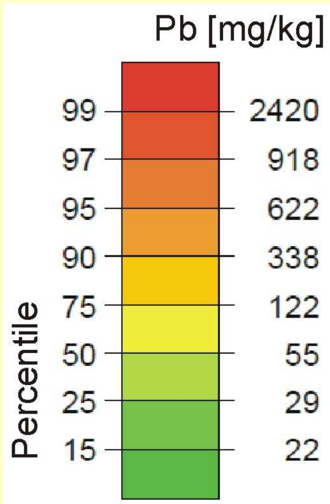


(total content)

2. Pb in top soils

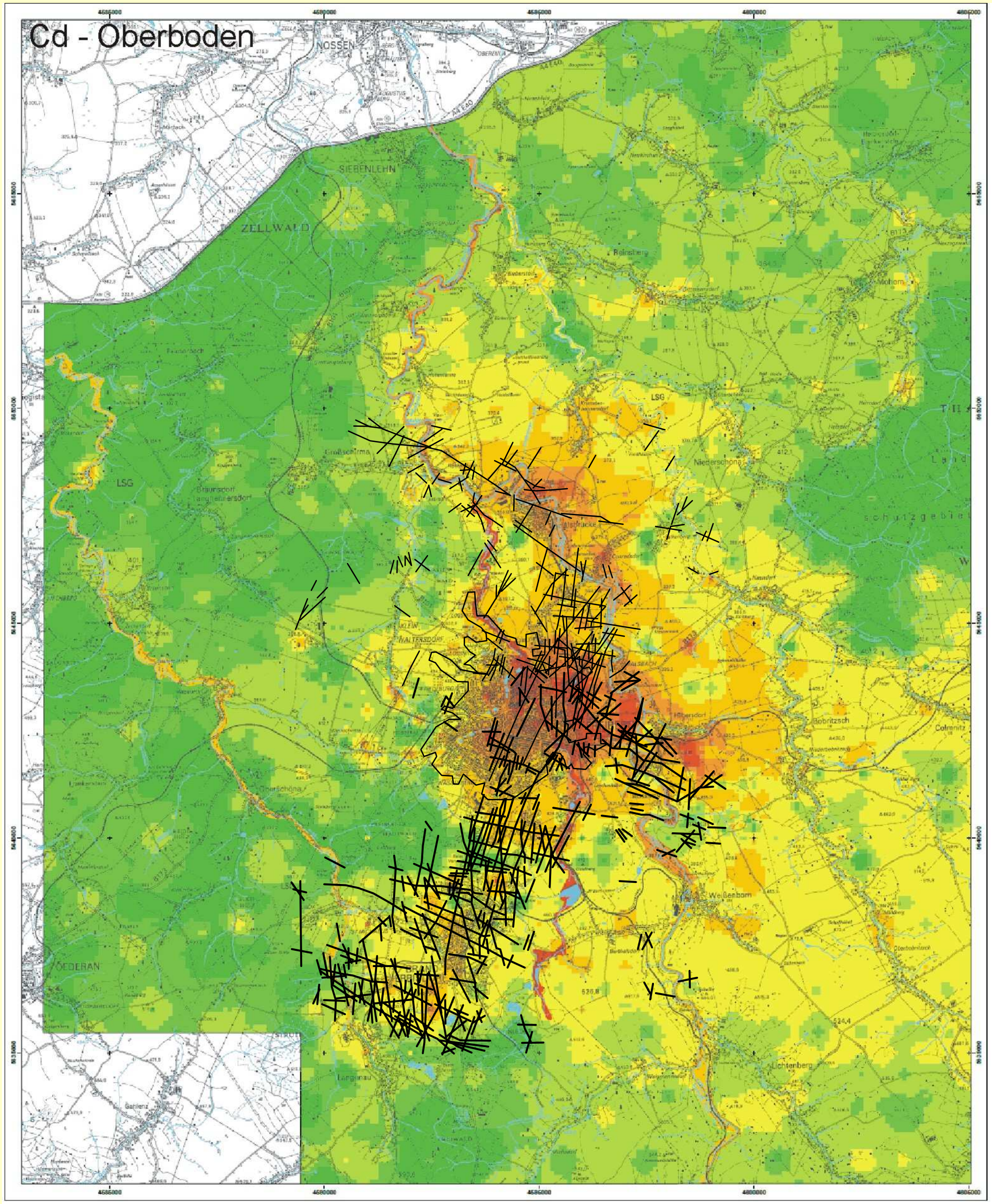


Data source:
Landesamt für Landwirtschaft,
Umwelt und Geologie Sachsen
(G. Rank, K. Kardel)

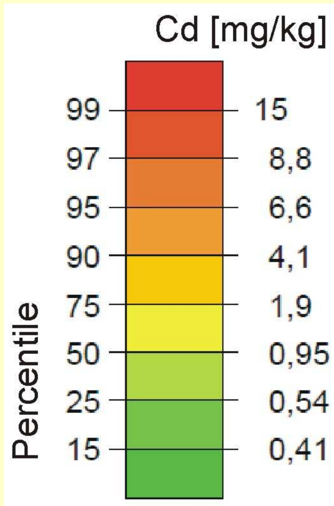


(total content)

2. Cd in top soils



Data source:
Landesamt für Landwirtschaft, Umwelt und Geologie Sachsen (G. Rank, K. Kardel)



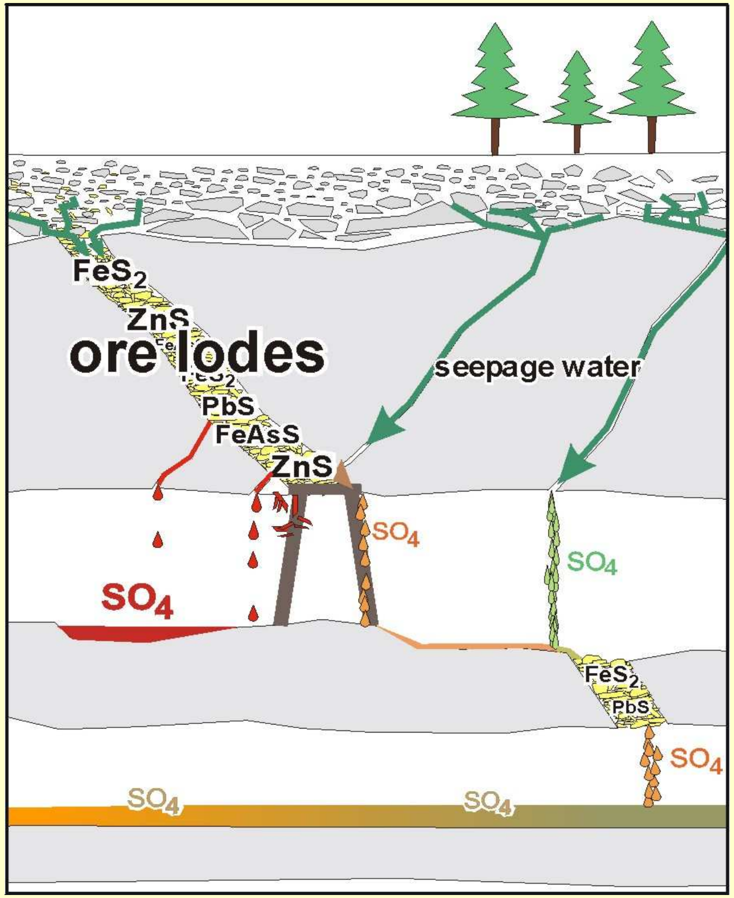
(total content)

2. Contamination sources of heavy metals/As

Problem: 800 years contamination of soils, water (sediments) with heavy metals and As by:

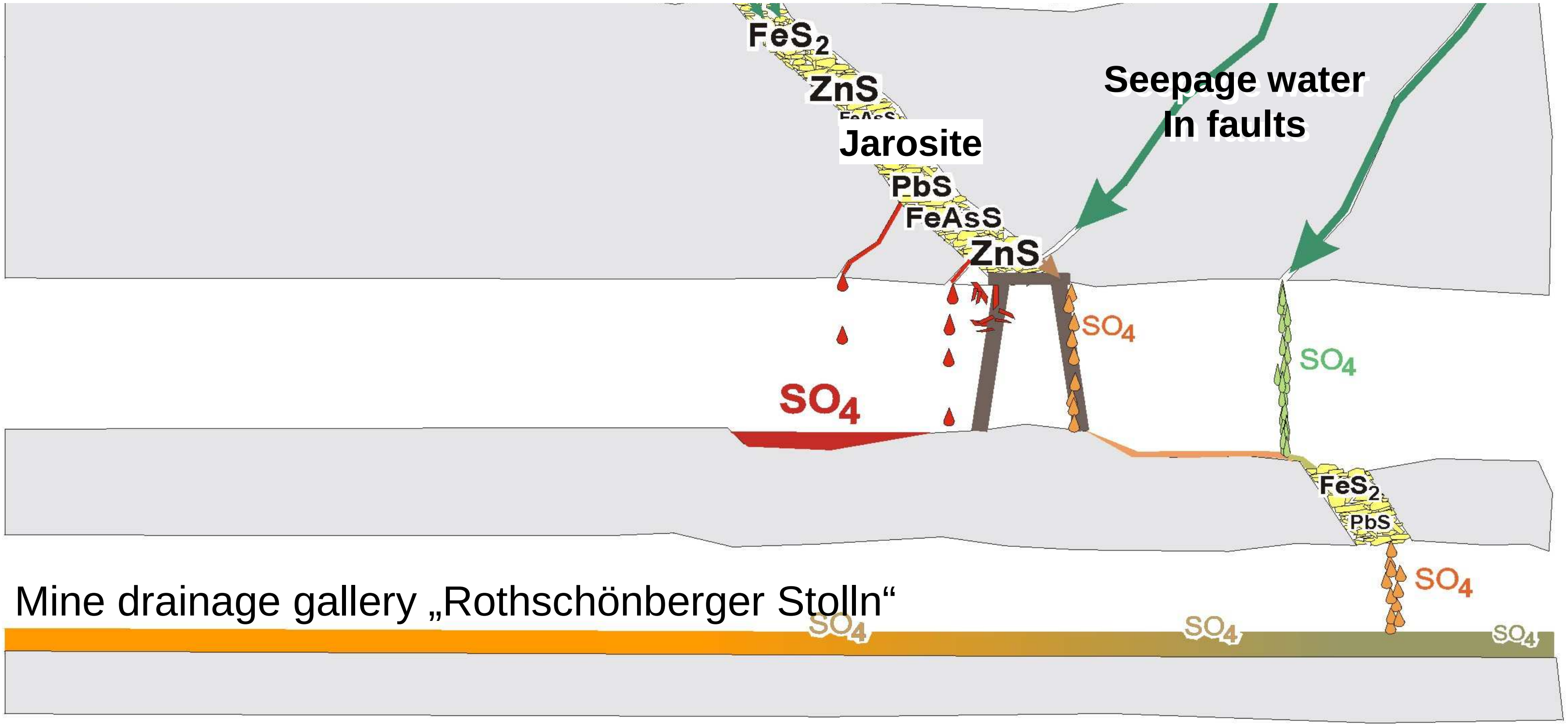
1. Natural ore lodes - geogenic background
2. Anthropogenic influence

- Old mining dumps
- Tailings of old smelteries
- Backfilled and embedded low grade ores (in the closed mine)



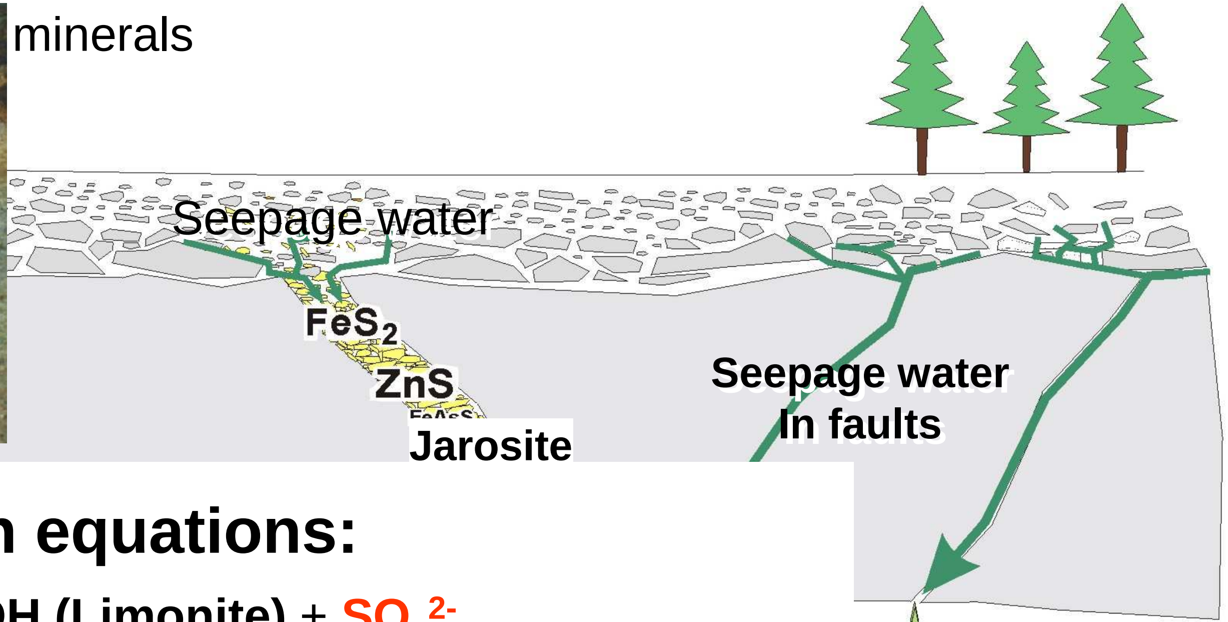
3. Backfilled and embedded low grad ores in old mine lodes

	Pb	Cu	Zn	Cd	As	Fe	Σ	S
weighted mean	8,5	0,8	14,3	0,1	2,2	31,9	**57,8**	**42,2**
	Proportions of metals to sulphur [%]							**[%]**



Mean percentage element content of main ore lodes

3. Backfilled and embedded low grad ores in old mine lodes



Simplified reaction equations:

FeS_2 + x O_2/H_2O → **FeOOH (Limonite)** + SO_4^{2-}

FeS_2 + x O_2/H_2O + K^+ → **$KFe_3[(OH)_6/(SO_4)_2]$ (Jarosite)** + x SO_4^{2-}

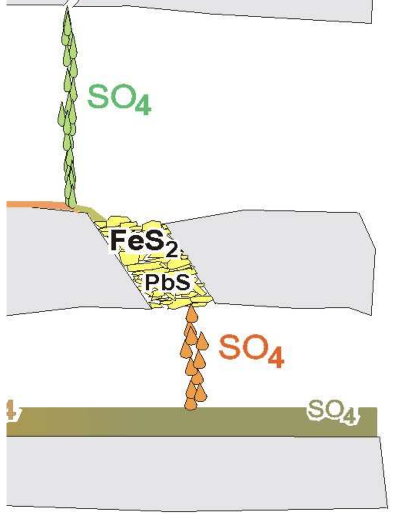
FeAsS + x O_2/H_2O → **$FeAsO_4$ x $2H_2O$ (Scorodite)** + SO_4^{2-}

PbS + x O_2/H_2O → **$PbSO_4$ (Anglesite)**

Ca^{2+} + SO_4^{2-} → **$CaSO_4$ x $2H_2O$ (Gypsum)**

Zn(Cd)S + x O_2/H_2O → Zn^{2+} + Cd^{2+} + SO_4^{2-} **(Solution)**

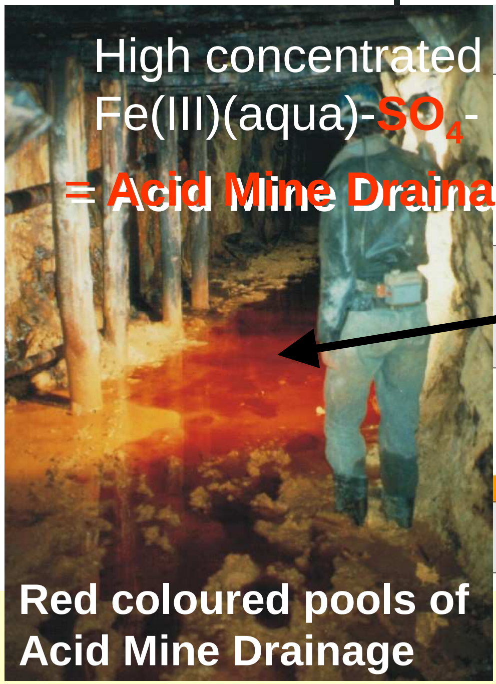
…

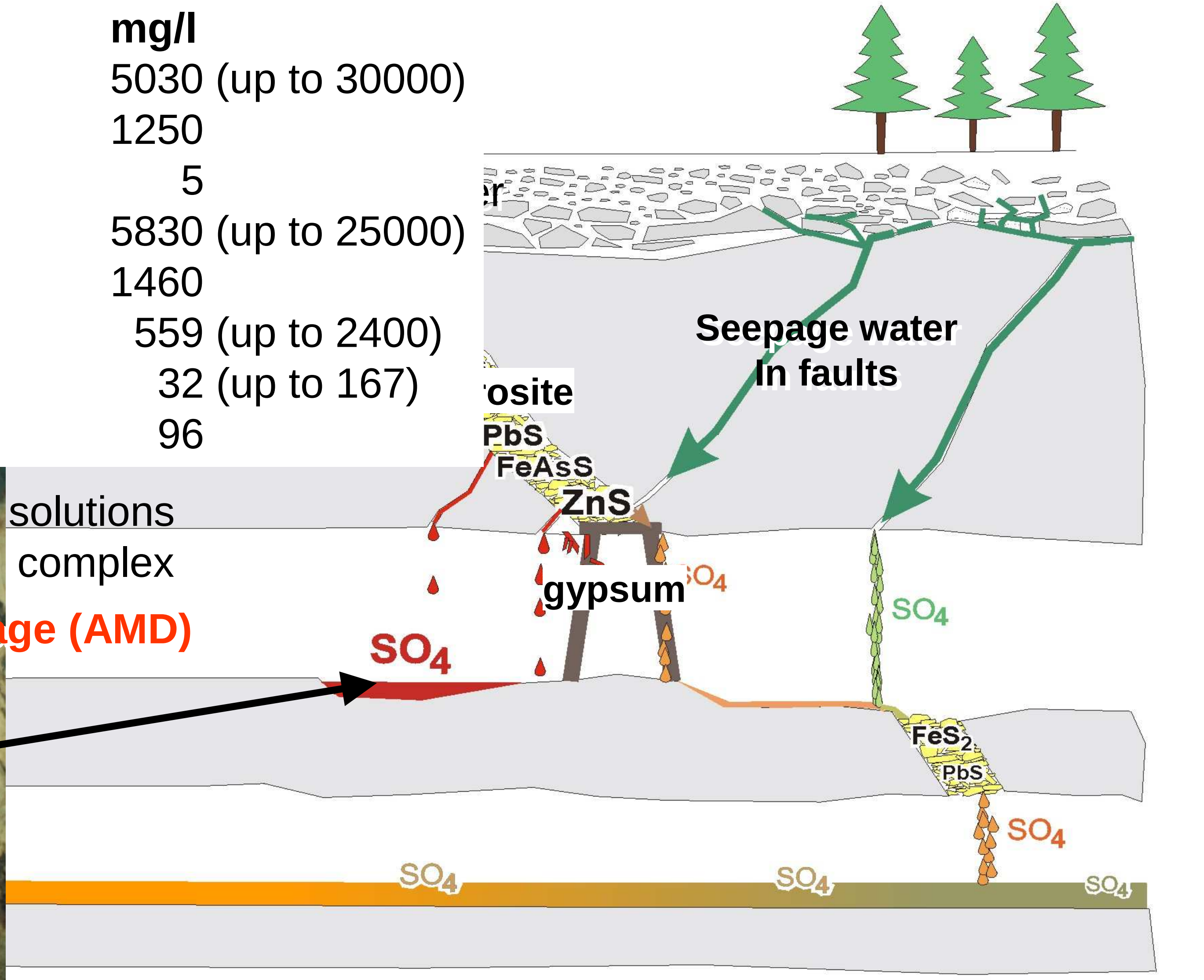


Oxidation of sulfide ores in the old mine „Reiche Zeche“ of Freiberg

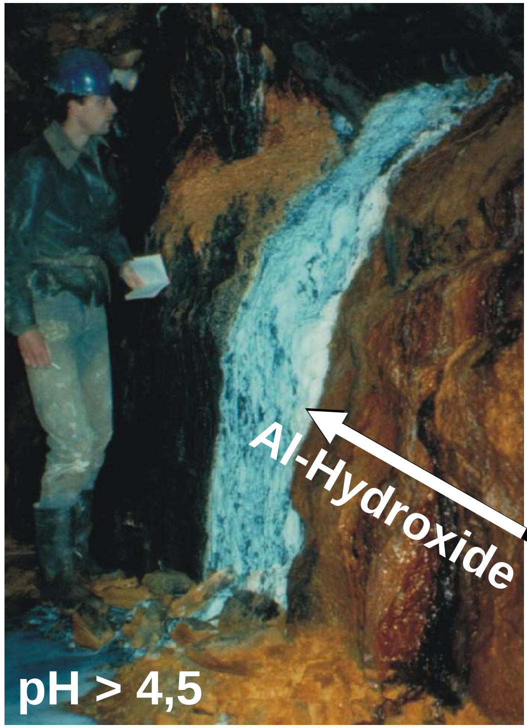
3. Typical element content of Acid Mine Drainage in Freiberg

	mg/l		mg/l
Ca^{2+}	26,5	Fe	5030 (up to 30000)
Mg^{2+}	1878	Mn	1250
Na^{+}	0,7	Pb	5
K^{+}	0,1	Zn	5830 (up to 25000)
Cl^{-}	50	Al	1460
SO_4^{2-}	32800	As	559 (up to 2400)
pH	**2,4**	Cd	32 (up to 167)
Lfgk 22,4 mS/cm		Cu	96





3. Precipitation processes in the mine



FeS_2
ZnS
PbS
$FeAsS$
$CuFeS_2$

Oxidation

Secondary minerals
(Jarosite, Anglesite, …)

Secondary minerals
(Jarosite, Gypsum, …)

AMD increase of pH

Precipitation of Fe- (adsorpt. Pb, As)
and Al-Hydroxides (adsorpt. Zn, Cd)

SO_4

metals

Deficit
between metals and sulphate

sulphate

Mine drainage gallery „Rothschönberger Stolln“

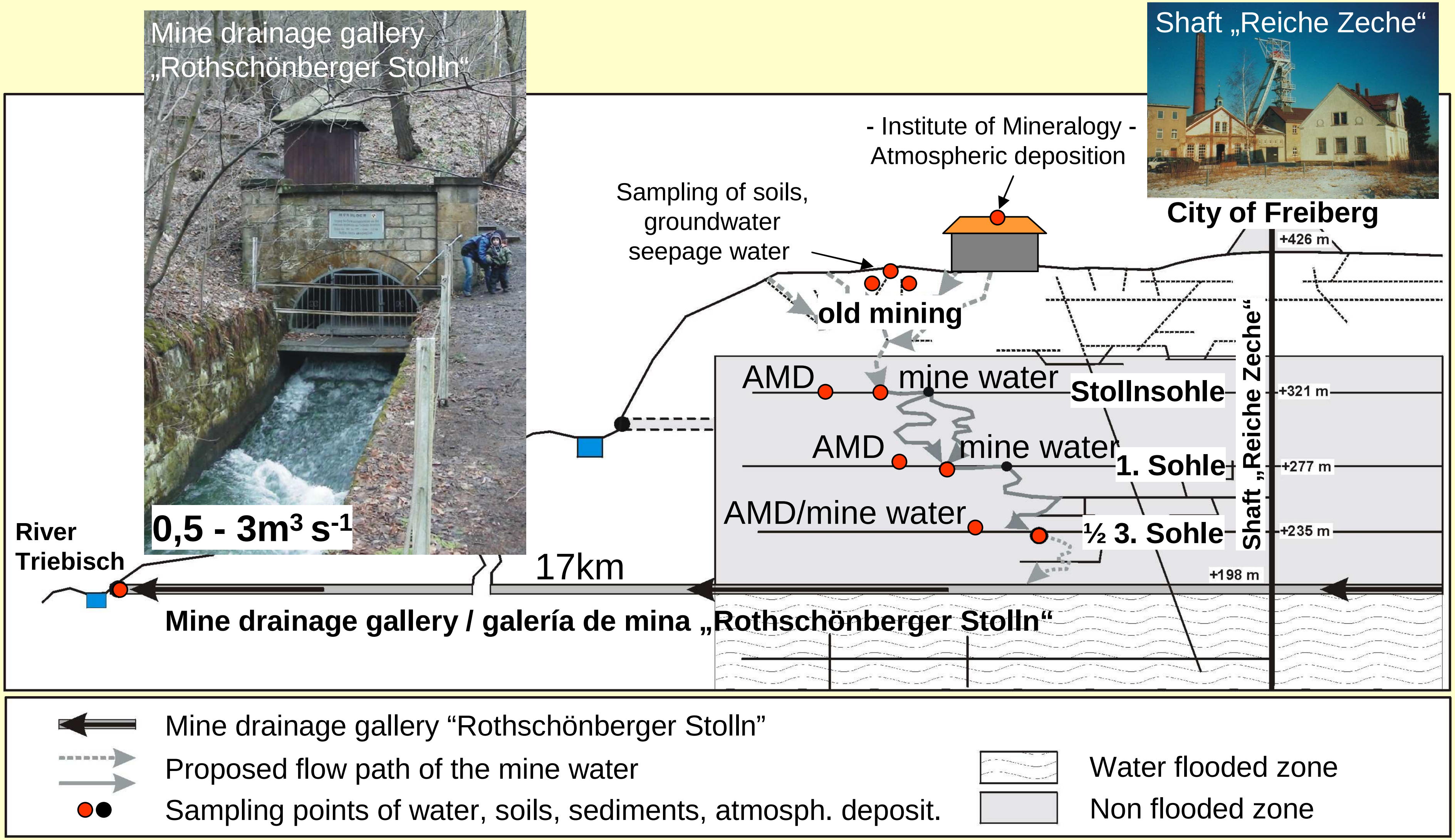
Our questions!

- How many tons of heavy metals/As from the oxidized sulphides were mobilised in the old mine ?
- What percentage of these heavy metals/As are sedimented as secondary minerals in the mine ?
- What percentage of these heavy metals/As are flushed out through the mine drainage gallery ?

Solution:

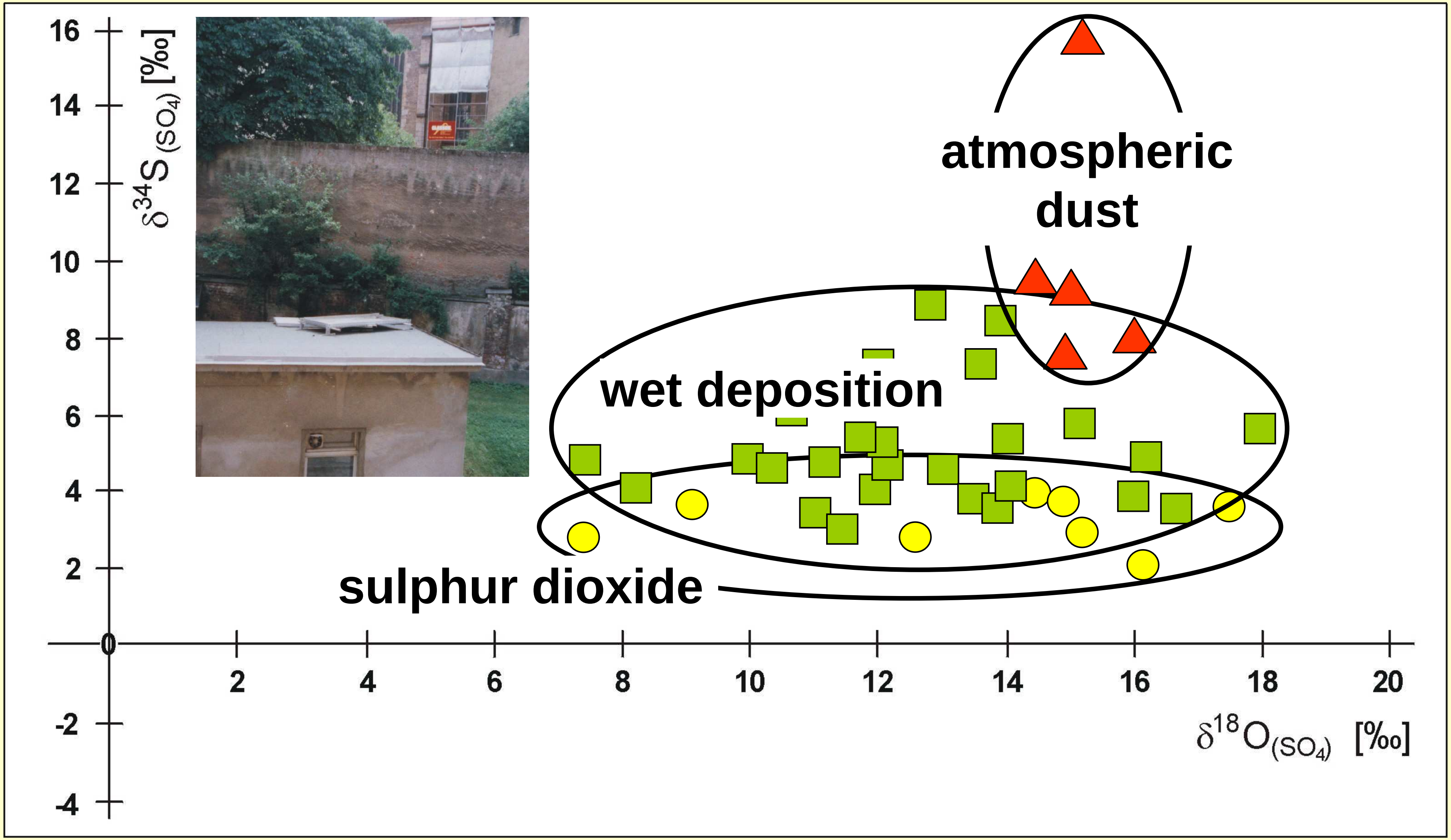
- Determination of ^{34}S and ^{18}O-Signatures of sulphides and sulphates in the environment and the mean percentage element content of main ore lodes

4. Follow up stable isotope of ^{34}S and ^{18}O of Sulphate from:



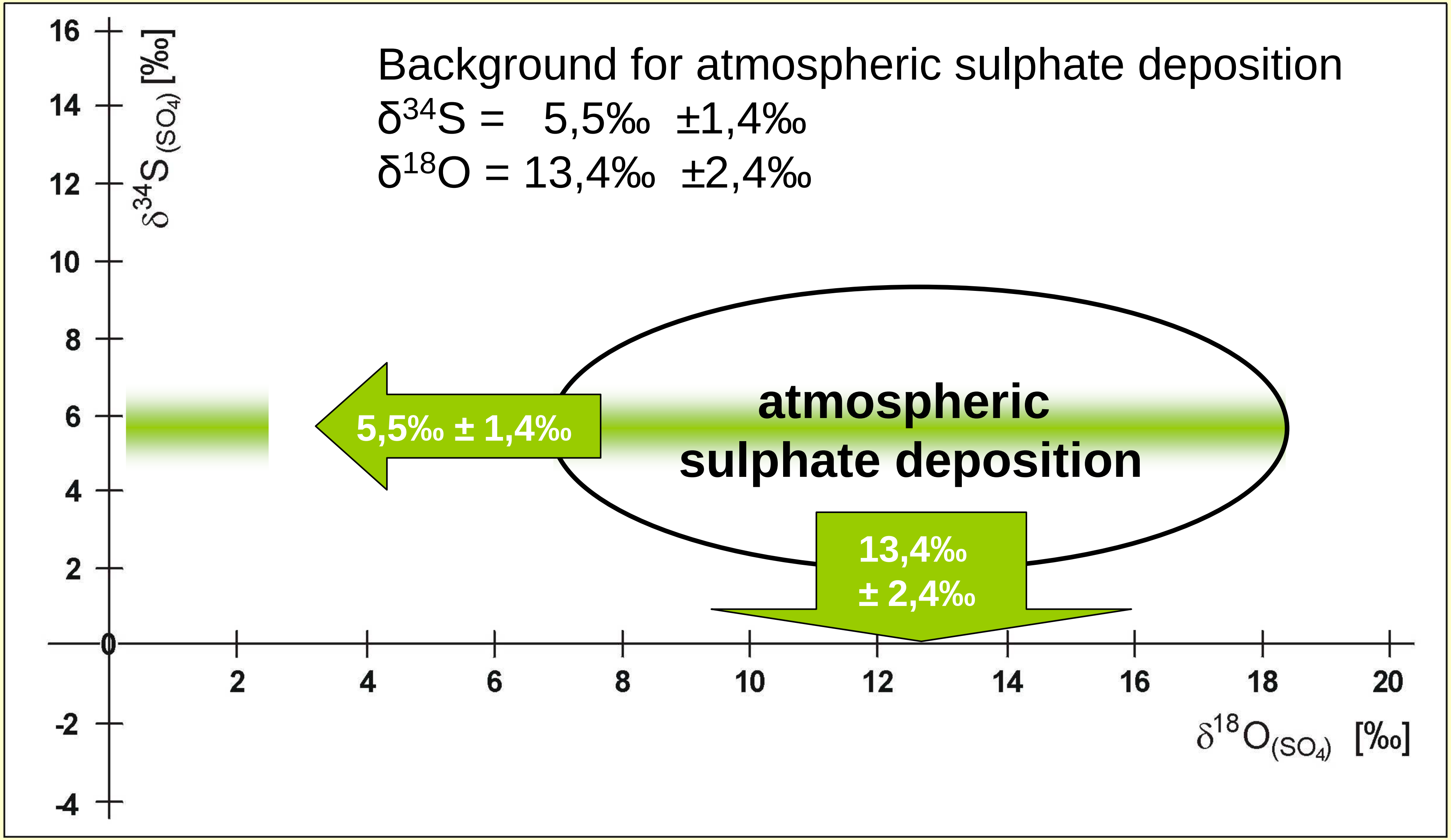
Cross section through the mine area of „Schwarzer Hirsch Stehender“ of the Freiberg polymetallic sulfide ore deposit and mine drainage gallery „Rothschönberger Stolln“

4. Isotopic composition of atmospheric sulphur components



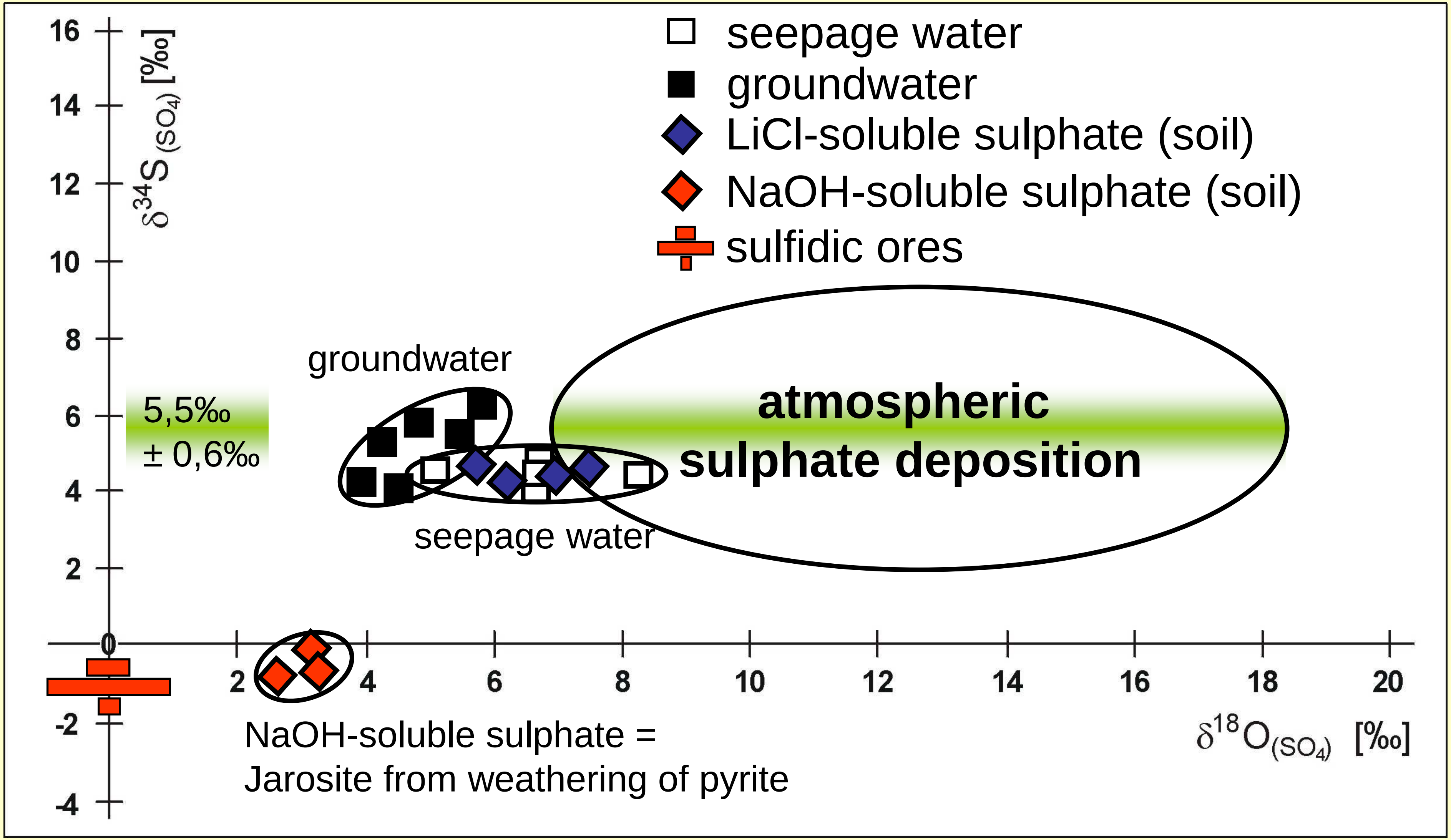
Sampling point at the „Institute of Mineralogie“ TU Bergakademie Freiberg

4. Isotopic composition of atmospheric sulphate deposition



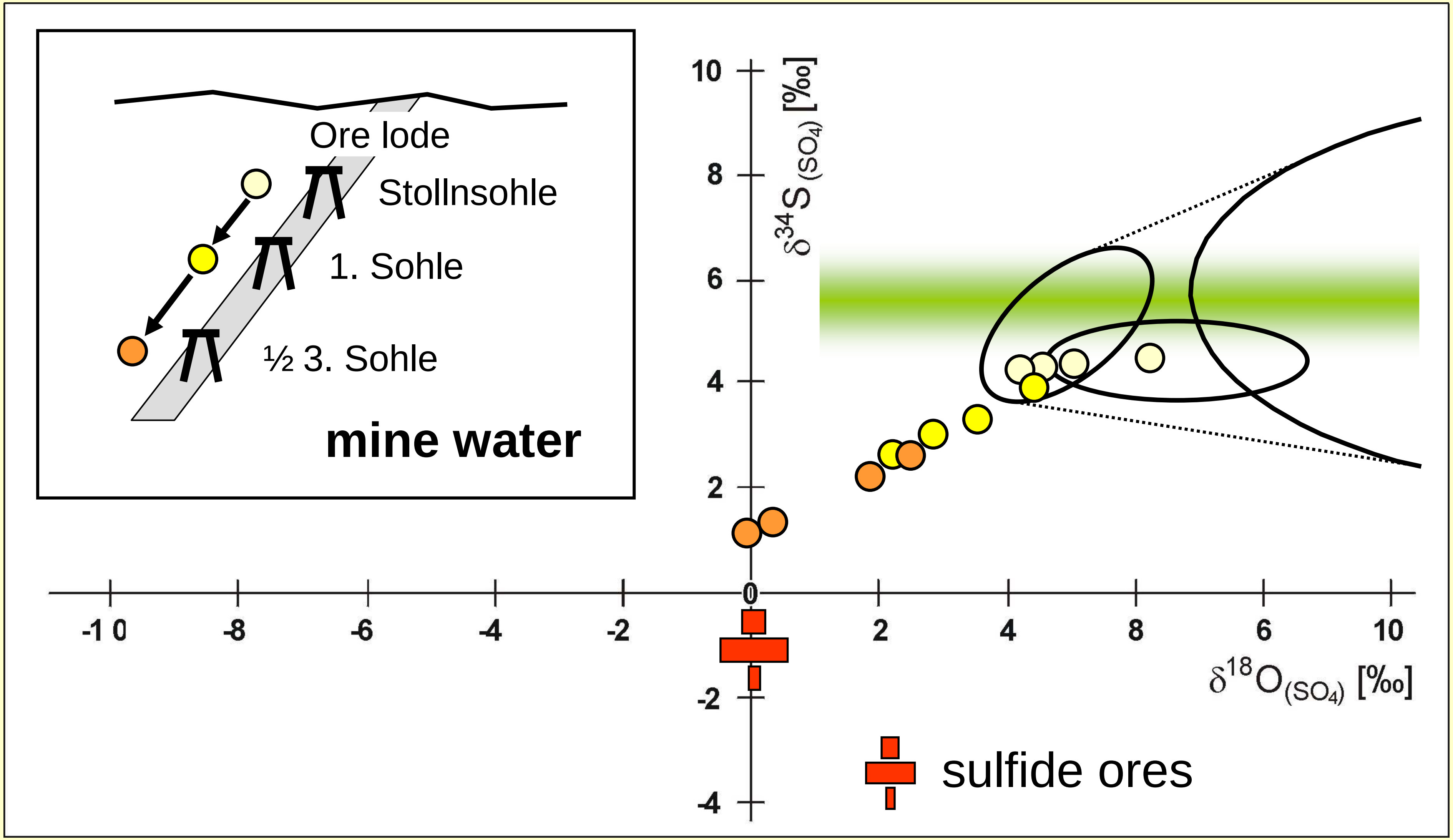
Sampling point at the „Institute of Mineralogie“ TU Bergakademie Freiberg

4. Isotopic composition of soils, ground- and seepage water



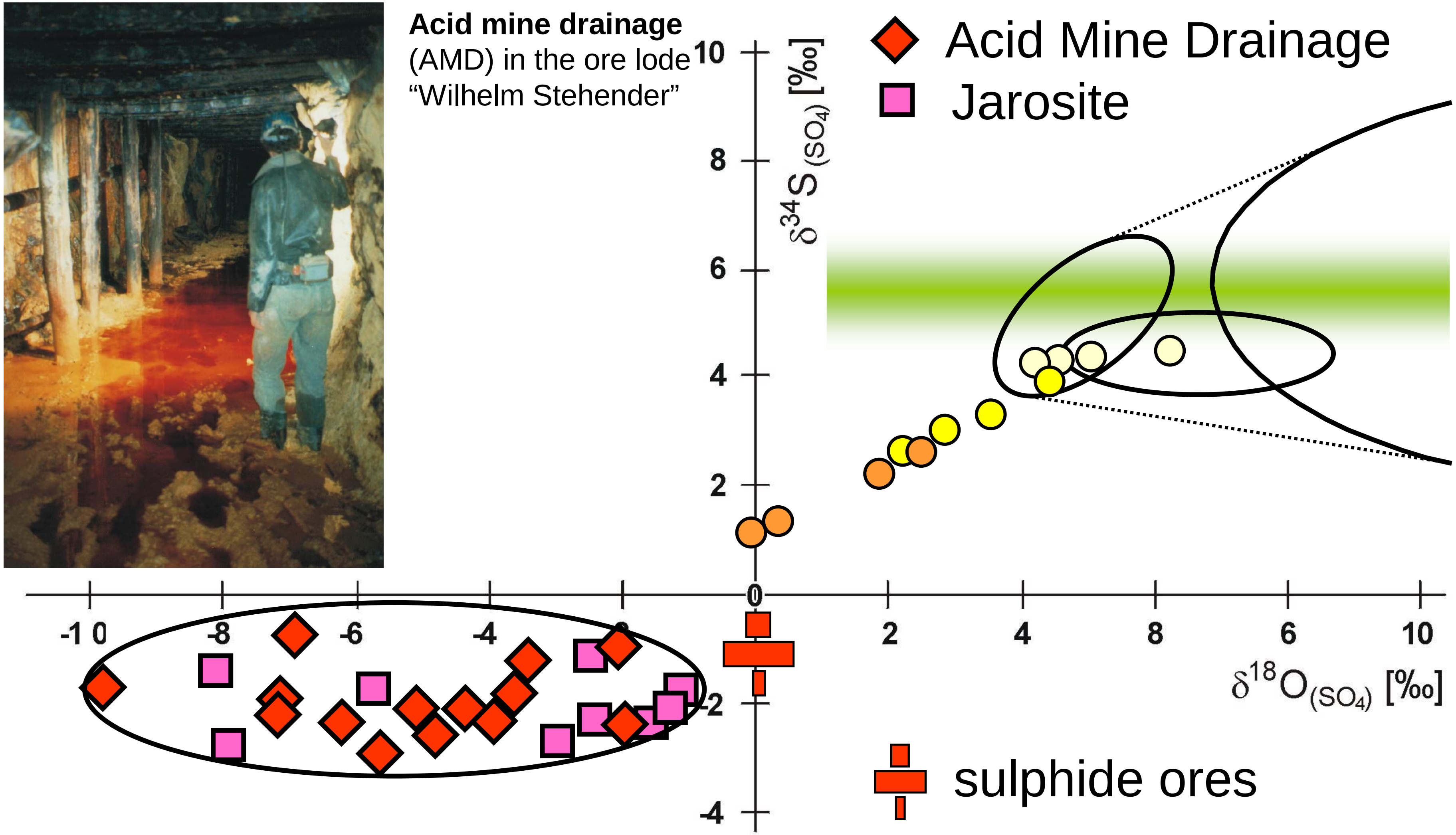
Sampling points near the shaft „Reiche Zeche“ Freiberg

4. Isotopic composition of sulphate of mine water



Sampling points ore lode „Schwarzer Hirsch Stehender“, Reiche Zeche

4. Isotopic composition of the Acid Mine Drainage - sulphates

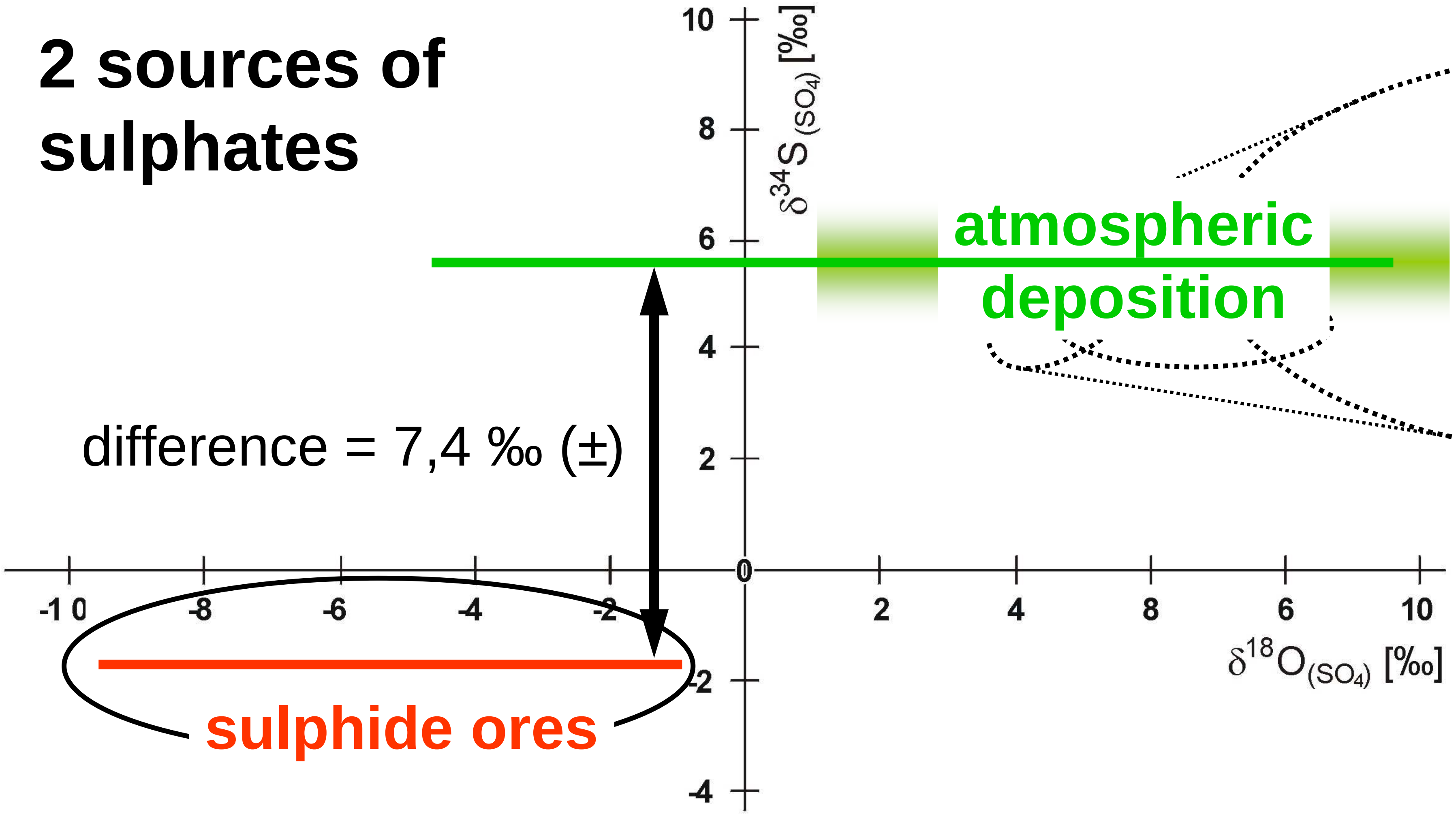


Acid mine drainage
(AMD) in the ore lode
“Wilhelm Stehender”

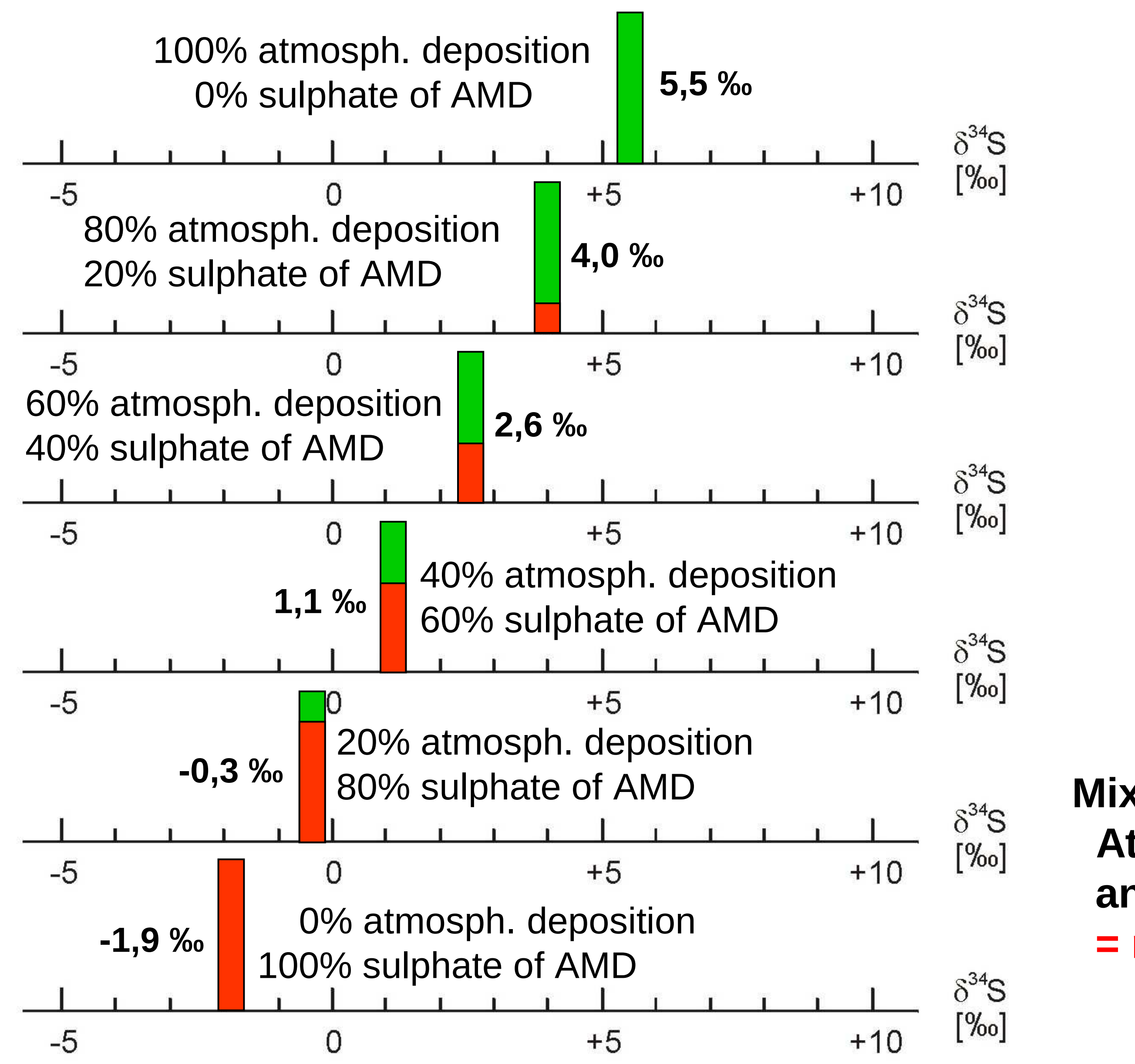
Sampling points ore lode „Schwarzer Hirsch Stehender“, Reiche Zeche

4. Sources of SO_4: atmospheric and from oxidized sulphides

2 sources of sulphates



4. Sulphate mixing line: atmospheric and from oxidized sulphides



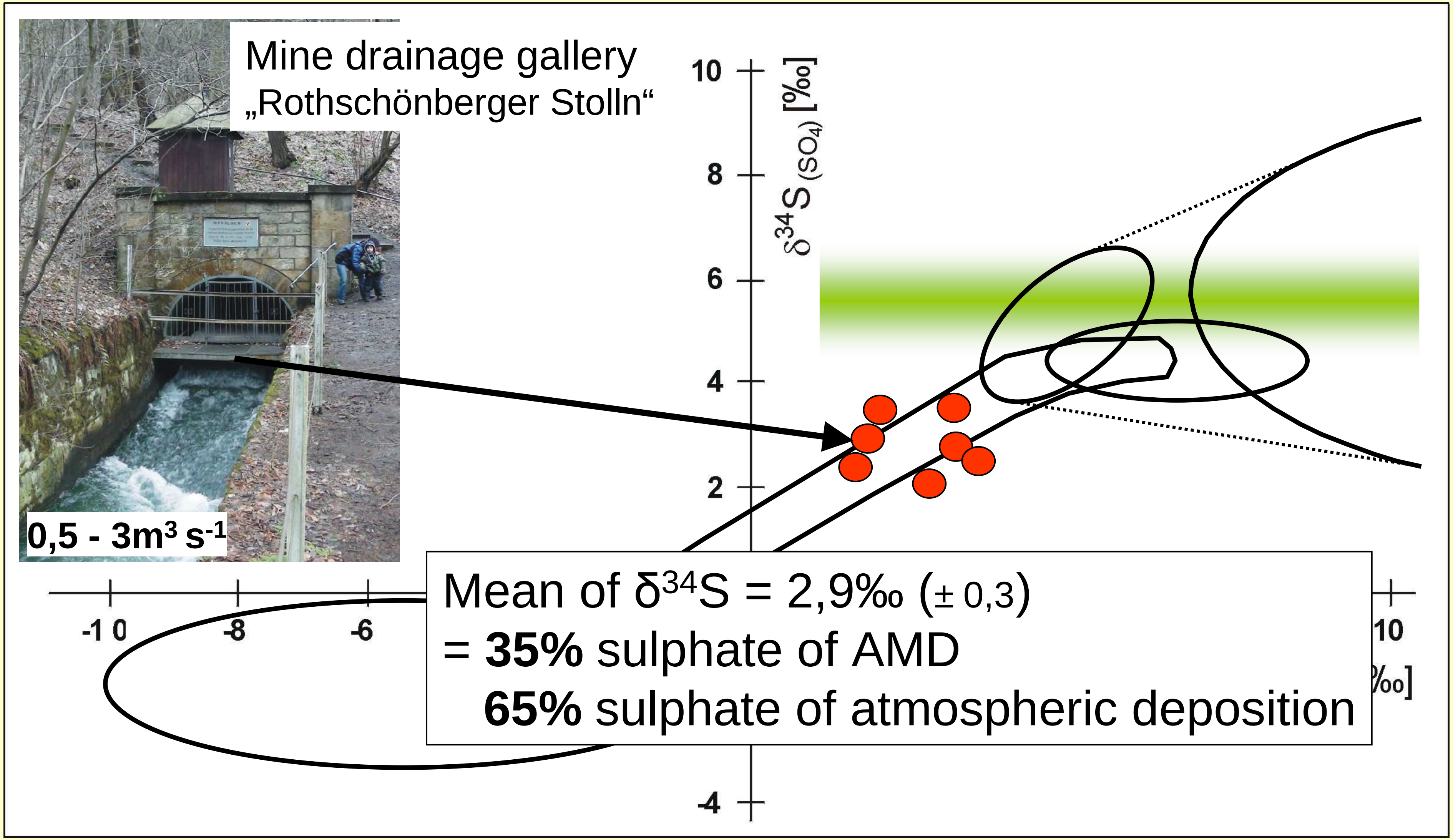
Initial value of the atmospheric sulphate (deposition) = 5,5 ‰ (± 0,6 ‰)

Initial value of the AMD-sulphates = -1,9 ‰ (± 0,9 ‰)

Mixing of both sulphates in the mine waters / drainage galleries

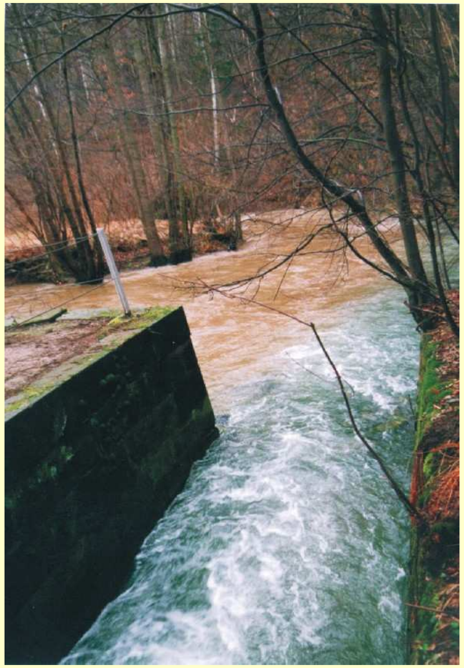
Mixing line of Atmospheric deposition and AMD-sulphates = mine water

4. Isotopic composition of sulphate of mine drainage gallery



Sampling point of the opening hole „Rothschönberger Stolln“

4. Calculation of minimum quantity of oxidized sulfide ores

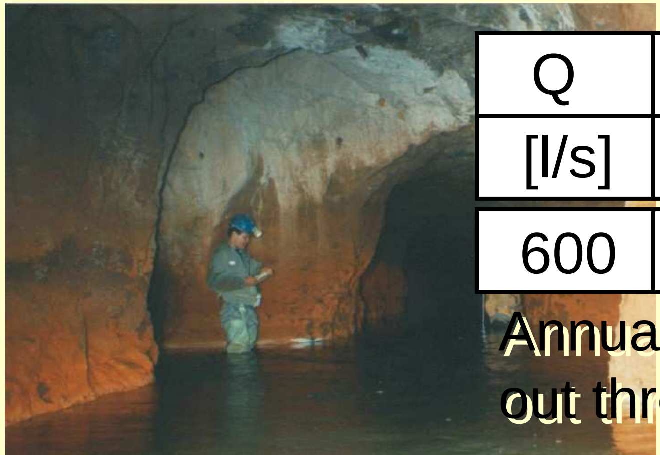


Rothschönberger Stolln
Opening hole

Pb	Cu	Zn	Cd	As	Fe	∑	S
8,5	0,8	14,3	0,1	2,2	31,9	**57,8**	**42,2**
Original main ore lodes (Proportions [%])							**[%]**

Q	Pb	Cu	Zn	Cd	As	Fe	S
[l/s]	[t/y]						
600	129	13	219	2,2	34	489	**1944**

Annually load of elements which is potentially flushed out through the mine drainage gallery



Rothschönberger Stolln near the shaft „Reiche Zeche“ (Photo: Kluge)

Q	Pb	Cu	Zn	Cd	As	Fe	S
[l/s]	[t/y]						
600	0,8	1,1	105	0,6	0,3	16,4	**6270**

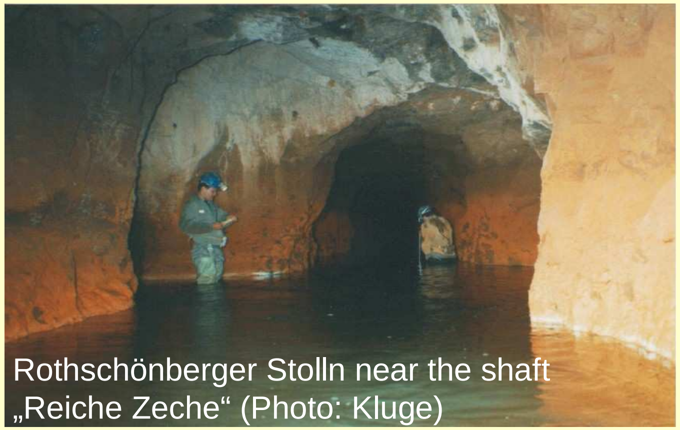
Annually load of elements which is really flushed out through the mine drainage gallery (include soluble and suspended matter)

4. Calculation of minimum quantity of oxidized sulfide ores


Sinter deposit (Photo: Kluge)


Fe-Hydroxide sinter deposit (Photo: Kluge)

	Pb [%]	Cu [%]	Zn [%]	Cd [%]	As [%]	Fe [%]
Flushed out (soluble+suspended matter)	0,6	8,9	ca. 50	ca. 70	0,8	3,4
Sedimented in the mine (sec. minerals)	99,4	91,1	ca. 50	ca. 30	99,2	96,6


Rothschönberger Stolln near the shaft „Reiche Zeche“ (Photo: Kluge)

Proportions between the really flushed out metal loads and the quantity of sedimented metals in the mine [%]

5. Conclusions

1. Two sources of sulphates for the Freiberg site were shown
- atmospheric sulphate
- sulphate from oxidized sulphide ores

Sulphates of mine waters are a mixing of both sources

2. Oxidation of low grade sulphide ores leads to formation of secondary minerals and high concentrated Acid Mine Drainage (AMD) - waters

3. Increasing of pH of AMD precipitate Fe- and Al-Hydroxides with adsorption of high quantities of Pb, As, Zn, Cd

4. The formation of secondary minerals and the adsorption of heavy metals on hydroxides (point 2 and 3) is a **„natural attenuation process“** of the environment

Gracias por atención
Thanks for attention
Vielen Dank