Natural attenuation processes of metals and sulphate in elder mining dumps/ tailings

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➢ Problem description

Mining activity ⇒ geochemical change ⇒ weathering of sulphides

AMD/ ARD- Phenomena ⇒ acidity (iron), trace metals, sulphate

ore mining ⇒ radionuclides, alkaline leaching

Prognosis ⇒ influence of dump waters to ground -/ surface waters

EUWRRL ⇒ Time-behaviour of source term, mass flow, trend reversal?

Process understanding ⇒ network of hydrobiogeochemical reactions

➢ Network of hydrobiogeochemical reactions

$FeS_2 + 3{,}5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2H^+$

$+O_2$ ↓ ↑ $+ Fe\ S_2$ (bei ph < 3- 3.5)

$Fe^{3+} + 3\ H_2O \leftrightarrow Fe(OH)_3 + 3\ H^+$

(bei ph > 3- 3.5)

Weathering circle

Carbonate buffer ⇒ **DIC, Ca^{2+}, Mg^{2+}, Fe^{2+}**

Cation exchange ⇒ **Na^+, K^+, Ca^{2+}, Mg^{2+}**

Al- u. Fe- hydroxide buffer ⇒ **Al^{3+}, Fe^{3+}, trace metals**

Alumosilicate-buffer ⇒ **Al^{3+}, H_2SiO_3, main Elements, trace metals**

Geogenic buffer potentials ⇒ storage pool of secondary minerals

➢Characteristics of the "mining bodies"

⇒ Very large source terms (comp. to organic pollutants)

- *No classical remediation as for org. pollutants possible*
- *only on Hot Spots remediation activities*

⇒ Process understanding of hydrogeochemical „reorganisation"

- *Balance of weathering*
- *Understanding of natural immobilisation (NA processes)*

⇒ Important ideas for reprocessing tailings

- *Structural understanding of metal-rich layers*
- *understanding of weathering zones*

Large network of research-projects „Controlled natural attenuation processes“ in Germany (called KORA) – funded by BMBF

⇒ **Leader of network No. 6**

⇒ **the Part „Mining bodies and Flood plain sediments“**

BMBF-Förderschwerpunkt **“Ko**ntrollierter natürlicher **R**ückhalt und **A**bbau von Schadstoffen in der Boden- und Grundwasserzone”

KORA

Themenverbund 6 “Bergbau und Sedimente”

➢ Network 6 - Mining bodies and flood plain sediments

6.1 – Flood plain sediments

- Anorganic (As, Cd) and organic pollutants - pesticides (DDX, HCH)
- TU Hamb.-Harb. (IUE), Fa. Dr.Fintelmann & Dr. Meyer

6.2 – Lignite opencast overburden dumps

- Immobilisation of acidity (sulphate, Fe, trace metals) by microbial sulphate reduction/ sulphide phase formation
- TUBAF, UFZ, GFI, G.E.O.S., INC

6.3 – Ore mining heaps/ Tailings

- Trace metal immobilisation – by crust formation at the capillary fringe (acidic & alkaline mining heaps)
- BGR Hannover, GFI Dresden

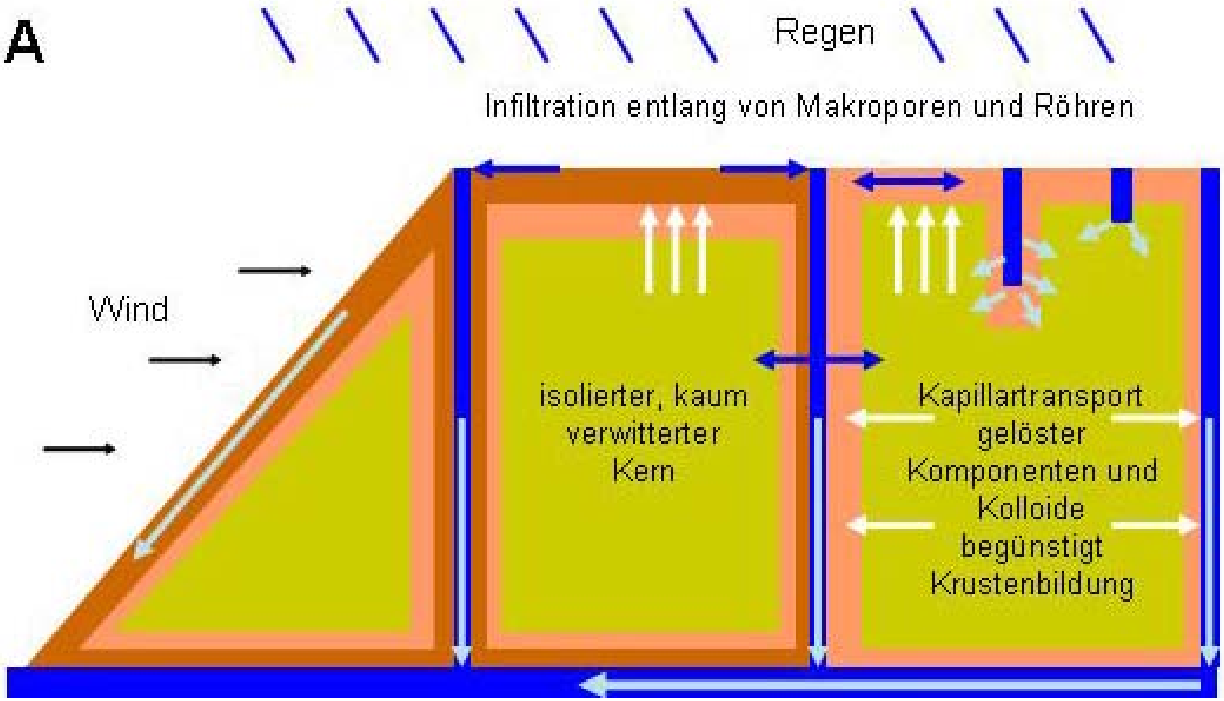
➢ Contents

Part A

Main results for ore mining heaps/ tailings

Th. Graupner (BGR Hannover), A. Kassahun (GFI Dresden), M. Furche (BGR Hannover), D. Rammlmair (BGR Hannover)

➢Crust formation at the capillary fringe



Crust formation by water infiltration/ mass transfer/ evaporation

Interplay of evaporation / chemical precipitation

Different kinds of crusts will be formed

⇒ Parts of the mining bodies sealed against flushing , mass transfer of trace metals is lowered

➢Types of crusts

Sulphidic Tailings (Freiberg)

Slag waste mining heap

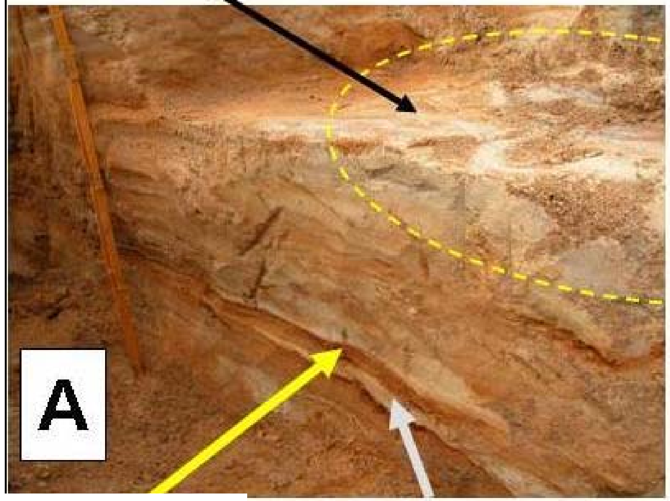
Importance of reactive materials (Glasses, feldspars, micas, ...)

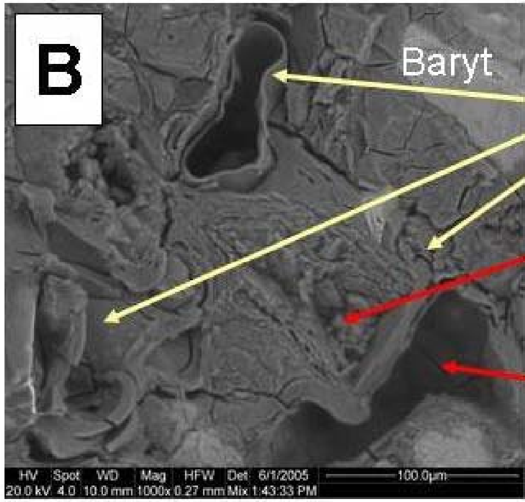
⇒ **Different types of crusts**

⇒ **well-known Fe(OH)-rich hardpan layers**

⇒ **Also Gel-phase crusts**

➢Types of crusts





Relevant types of mining heaps

⇒ **fine grained materials or glass-/ sediment mixtures**

⇒ **layer-like distributed reactive materials**

Non-relevant types of mining heaps

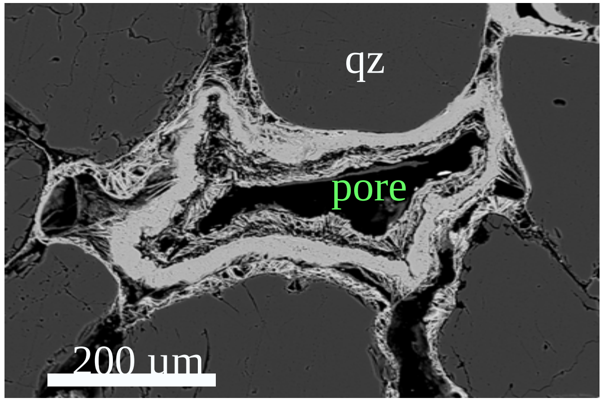
⇒ **Homogeneous grain-size and material distribution**

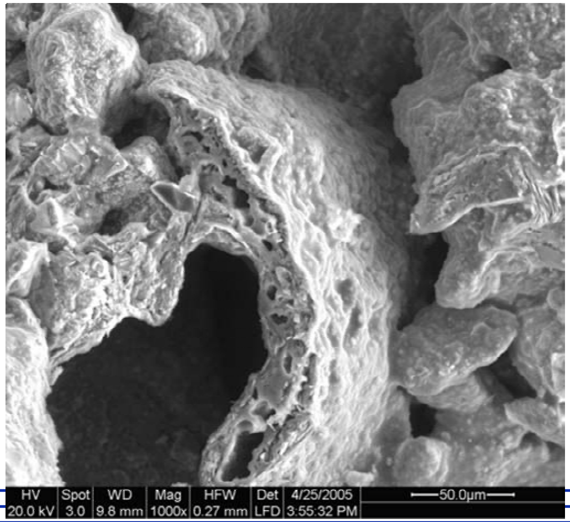
➢Si- Gel rich crusts – process understanding

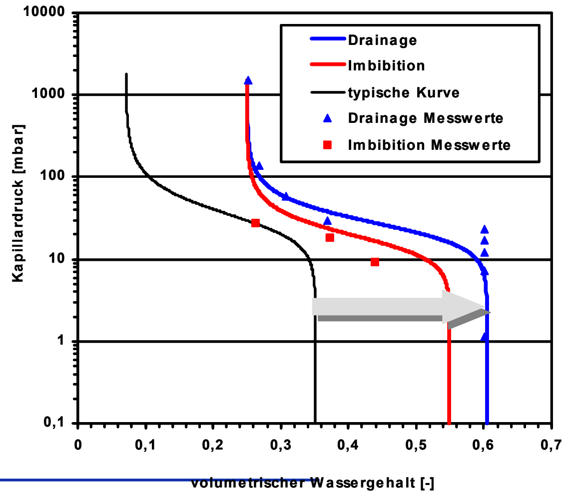
⇒ Gel formation by CO_2-influence, colloidal silica acid, polymerisation

⇒ Si-gel rich crusts leads to a shift in water retention behaviour

⇒ Gel formation – self-enhancing process and enrichment with metals





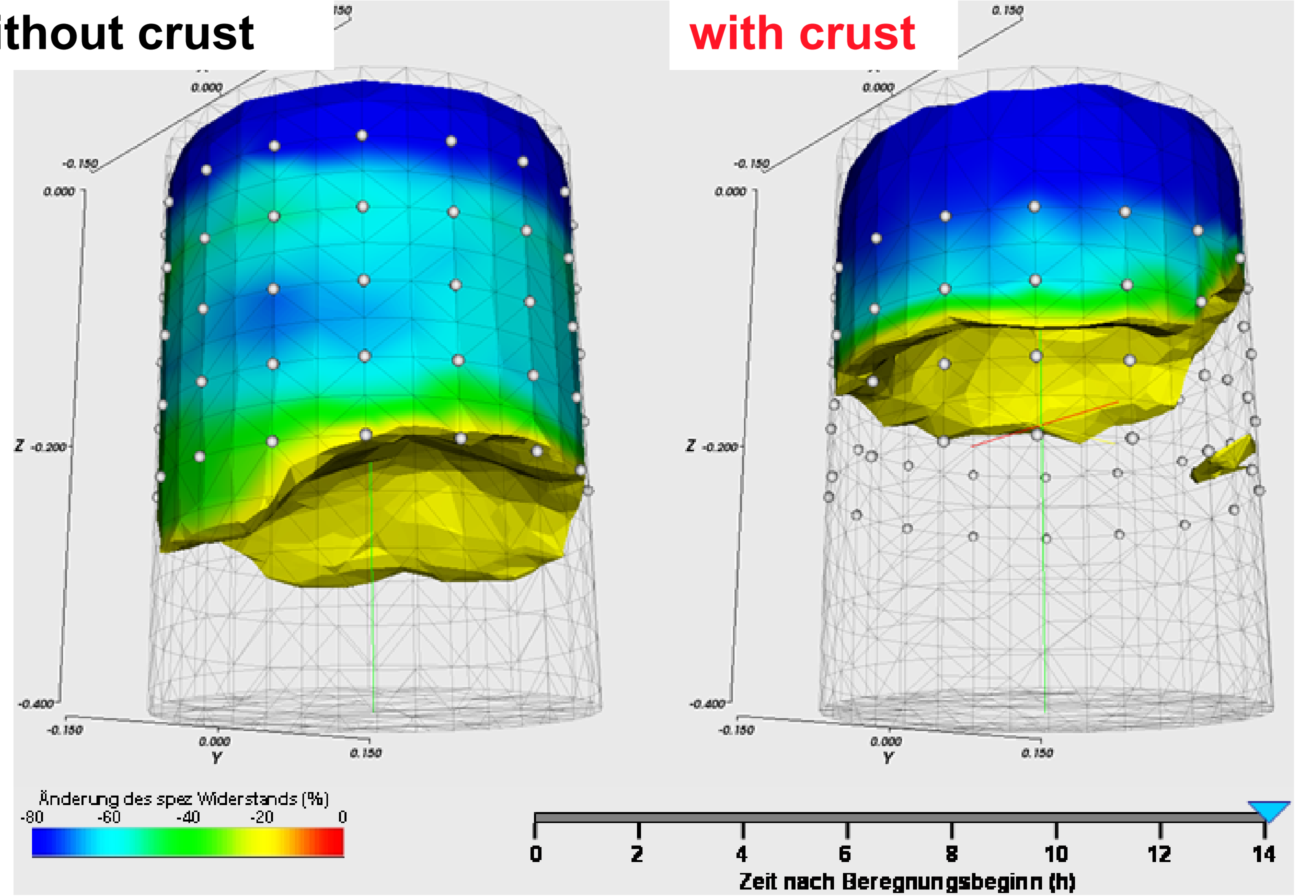


➢ Geoelectrical tomography – column tests

Comparison of heap material (iron slag) with crust and without crust (in-situ sampled)

➢ Geoelectrical tomography – results of column tests

without crust | with crust

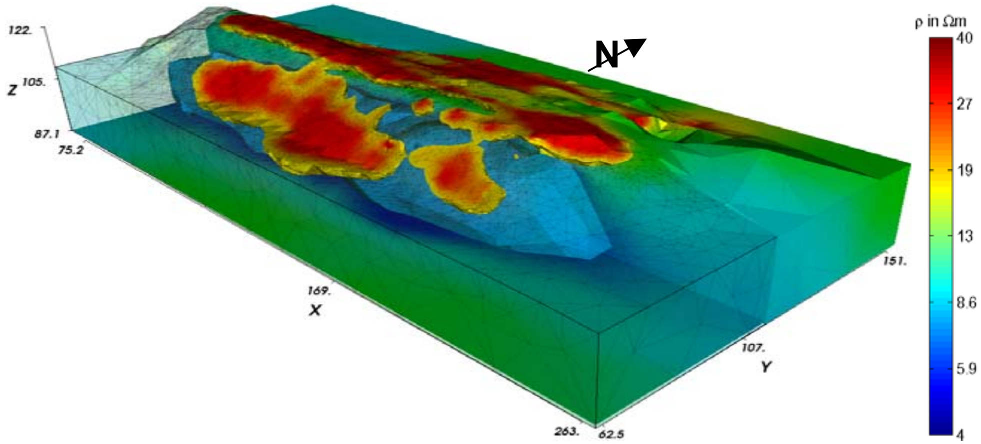


Continuously Sprinkling- / Drying- experiment:

Water front after „Sprinkling“ infiltrated with crust much less

Evaporation and ongoing crust formation take place

➢Geophysical monitoring system



Distribution of electrical resistivity
(DC3DTopo, T. Günther & C. Rücker)

⇒ **Geophysical monitoring system was developed and proved (Geoelectrics and Spectral Induced Polarisation)**

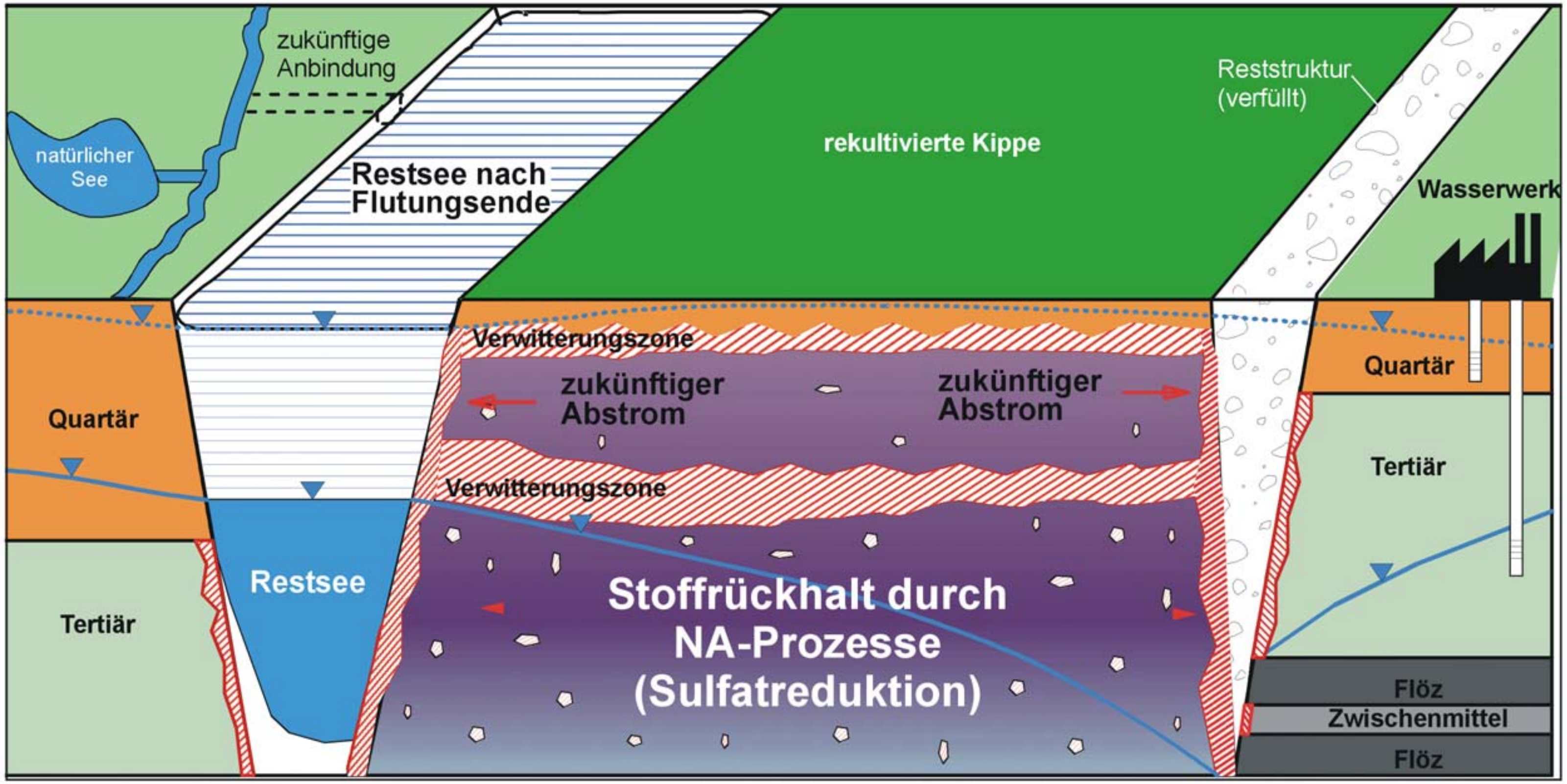
⇒ **Showing the evidence of crusts is possible**

Part B

Main results for lignite overburden dumps

(**TUBAF**,GFI,UFZ, GEOS, INC)

➢Detailed problem description



- ⇒ **open cast – AMD generation (acidity, iron, sulphate, trace metals)**
- ⇒ **network of hydrobiogeochemical reactions**
- ⇒ **microbial sequence of reduction reactions**
- ⇒ **“Engine” = dumped tertiary C_{org}**

➢ Geflecht von hydrobiogeochem. Reaktionen

Carbonate buffer ⇒ **DIC, Ca^{2+}, Mg^{2+}, Fe^{2+}**

Cation exchange ⇒ **Na^+, K^+, Ca^{2+}, Mg^{2+}**

Al- u. Fe- hydroxide buffer ⇒ **Al^{3+}, Fe^{3+}, trace metals**

Alumosilicate-buffer ⇒ **Al^{3+}, H_2SiO_3, main Elements, trace metals**

$FeS_2 + 3{,}5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2H^+$

$+O_2$

$+ Fe\ S_2$ (bei ph < 3- 3.5)

$Fe + 3\ H_2O \leftarrow Fe(OH)_3 + 3\ H^+$

(bei ph > 3- 3.5)

Weathering circle

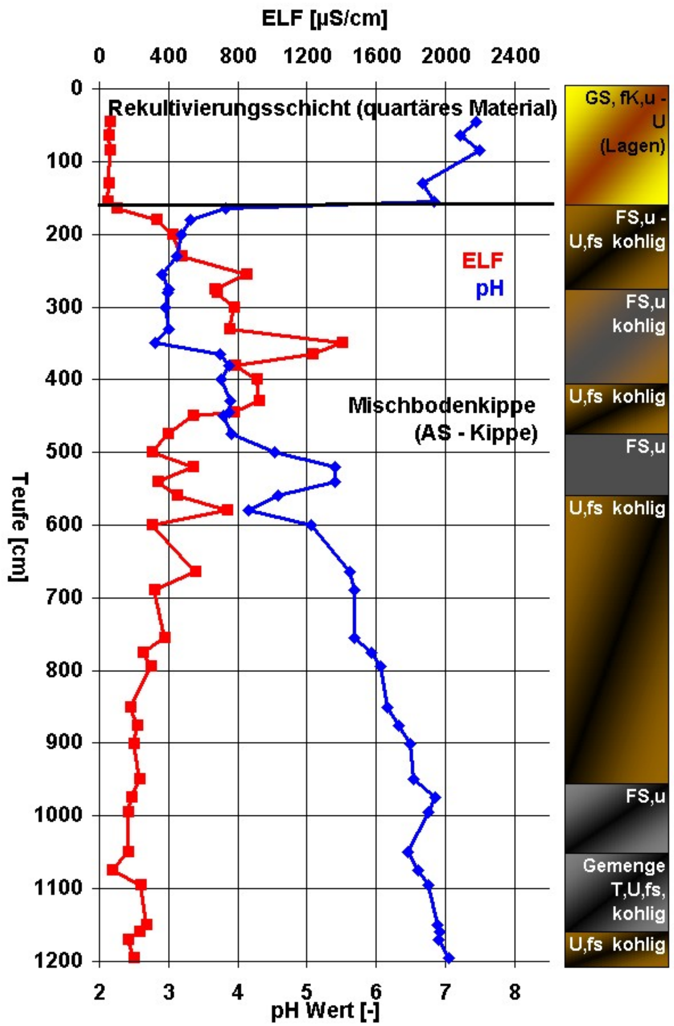
Geogenic buffer potentials ⇒ storage pool of secondary minerals

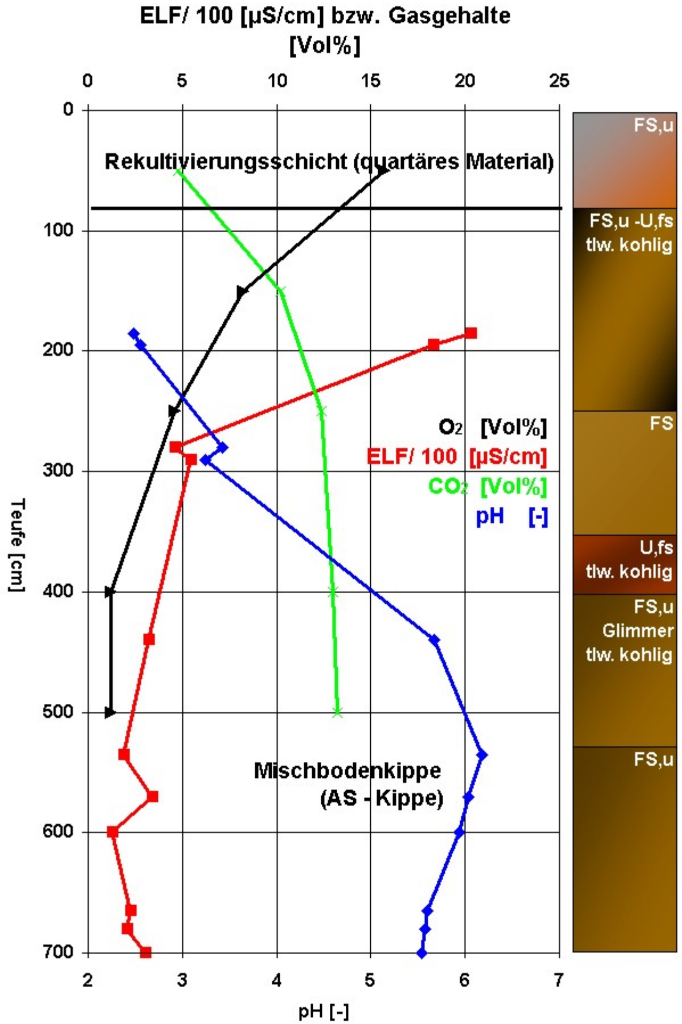
Microbial redox sequence ⇒ transformation of tertiary C_{org}

aerobe respiration	$CH_2O + O_2 \rightarrow CO_2 + H_2O$
Nitrate reduction	$CH_2O + 0{,}5\ NO_3^- + H^+ \rightarrow CO_2 + 0{,}5\ N_2 + 0{,}5\ H_2O$
Manganese reduction	$CH_2O + 2\ MnO_2(s) + H^+ \rightarrow CO_2 + 2\ Mn^{2+} + 0{,}5\ H_2O$
Iron reduction	$\mathbf{CH_2O + 4\ FeOOH(s) + 8\ H^+ \rightarrow CO_2 + 7\ H_2O + 4\ Fe^{2+}}$
Sulphate reduction	$\mathbf{CH_2O + 0{,}5\ SO_4^{2-} + 0{,}5\ H^+ \rightarrow 0{,}5\ HS^- + CO_2 + H_2O}$
Methane fermentation	$CH_2O \rightarrow 0{,}5\ CH_4^- + 0{,}5\ CO_2$

➤NA-Indicators for lignite overburden dumps

Field-Investigations of elder dumps – ca. 60 years (TUBAF [2000])



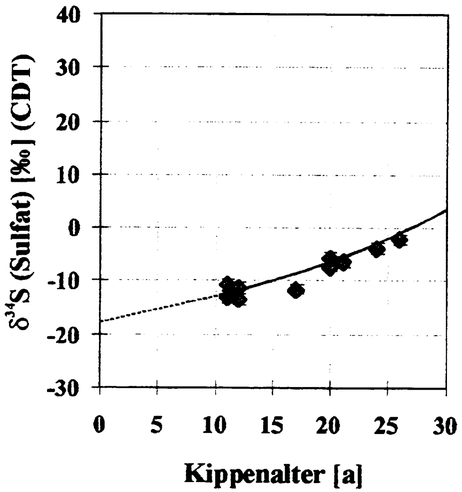


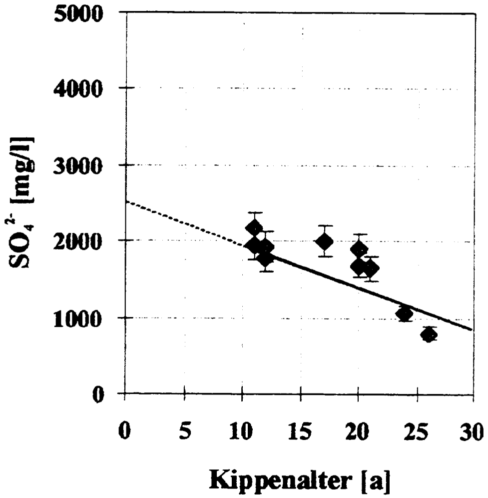
➢NA-Indicators for lignite overburden dumps

Field-Investigations of elder dumps (TUBAF [2000], UFZ [1999])

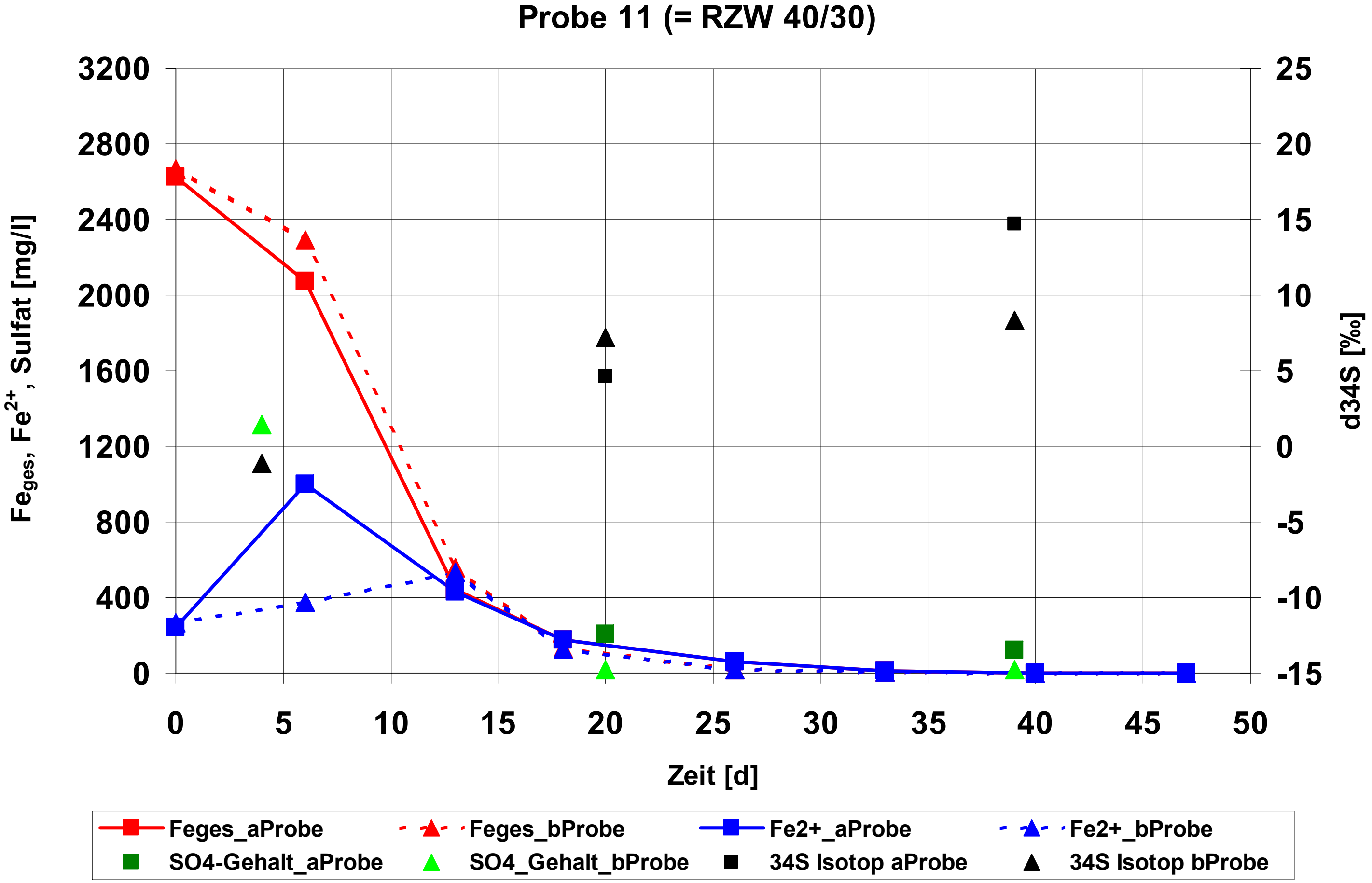
⇒ **Activatability of SRB (dump ground waters)**

⇒ **Sulphate isotopic values (dump ground waters)**





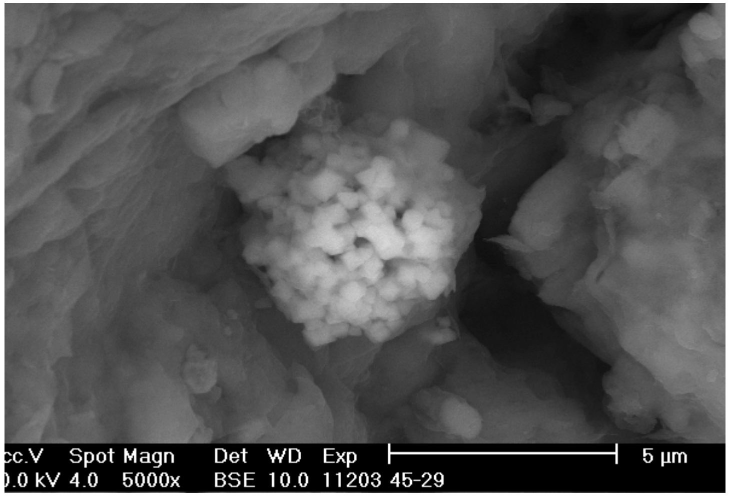
➢ Tests (ideal) with autochthonic biocenosis

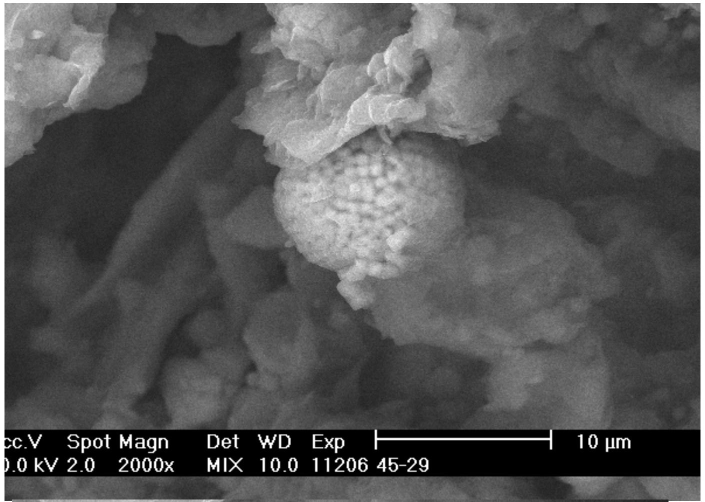


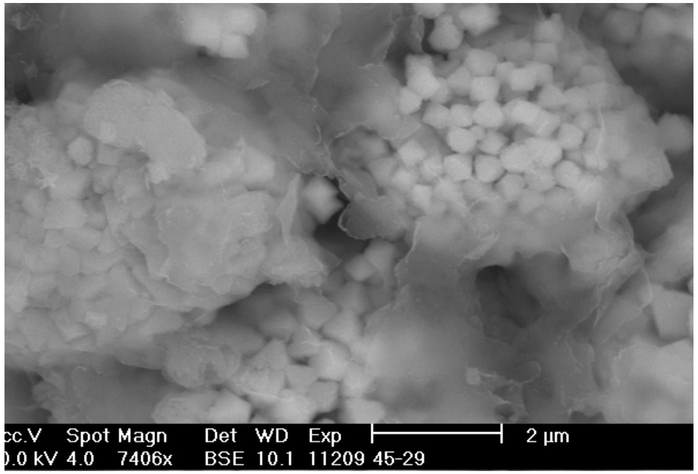
⇒ Fe-/ Sulphate-reduction „sequential parallel“, very fast (high rates)

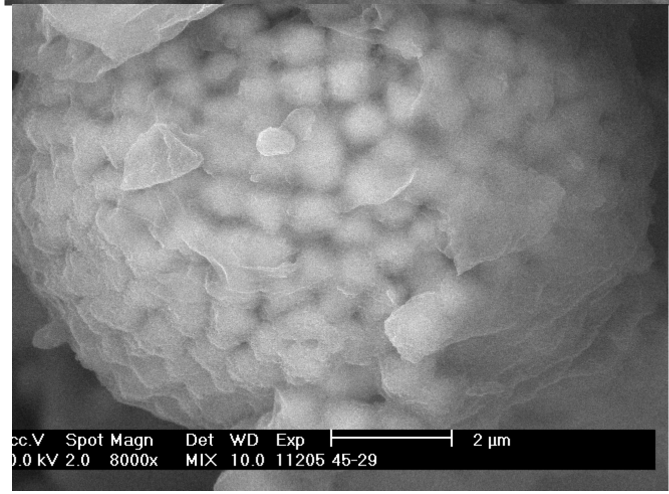
⇒ sterile controls ⇒ Main part is microbial process

➤SEM – new formed sulphides









SEM-investigation by Gert Schmidt (TUBAF-IKGB)

⇒ **Framboidale, partly amorphe structures (Greigit)**

⇒ **Variable Fe/S-ratios**

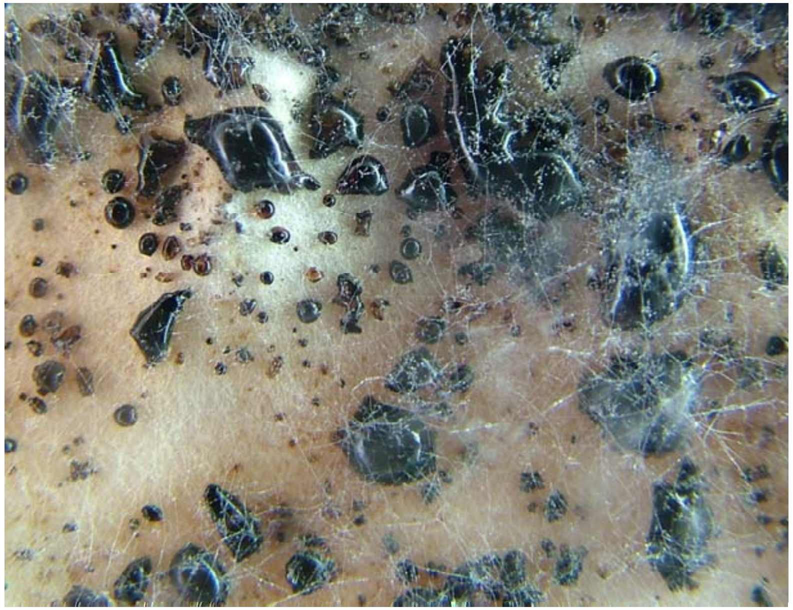
➢Tertiary C_{org} – Engine of the process sequence

⇒ **Dumped „residual coal“ (tert. C_{org}) – *available by partly oxidation***

⇒ **Cultivation of autochthonic fungies on site material**

⇒ **Liquification starts already after 5 days**

⇒ **up to 19 g/l DOC (humic substances - high masses, aromaticity)**



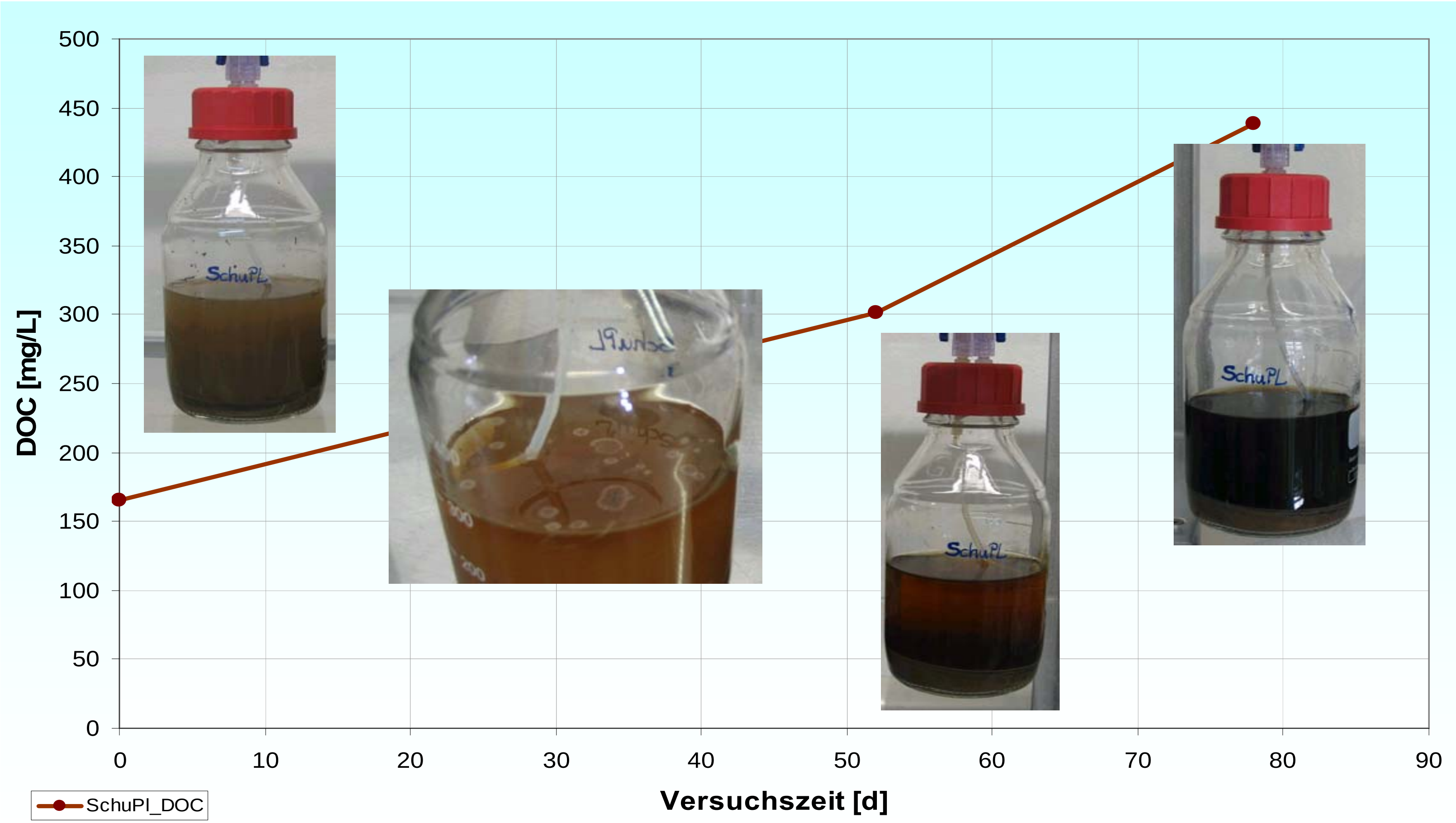
Dump ground waters show other behaviour

⇒ **Sign for microbial transformation**

⇒ **Important for microbial process engineering**

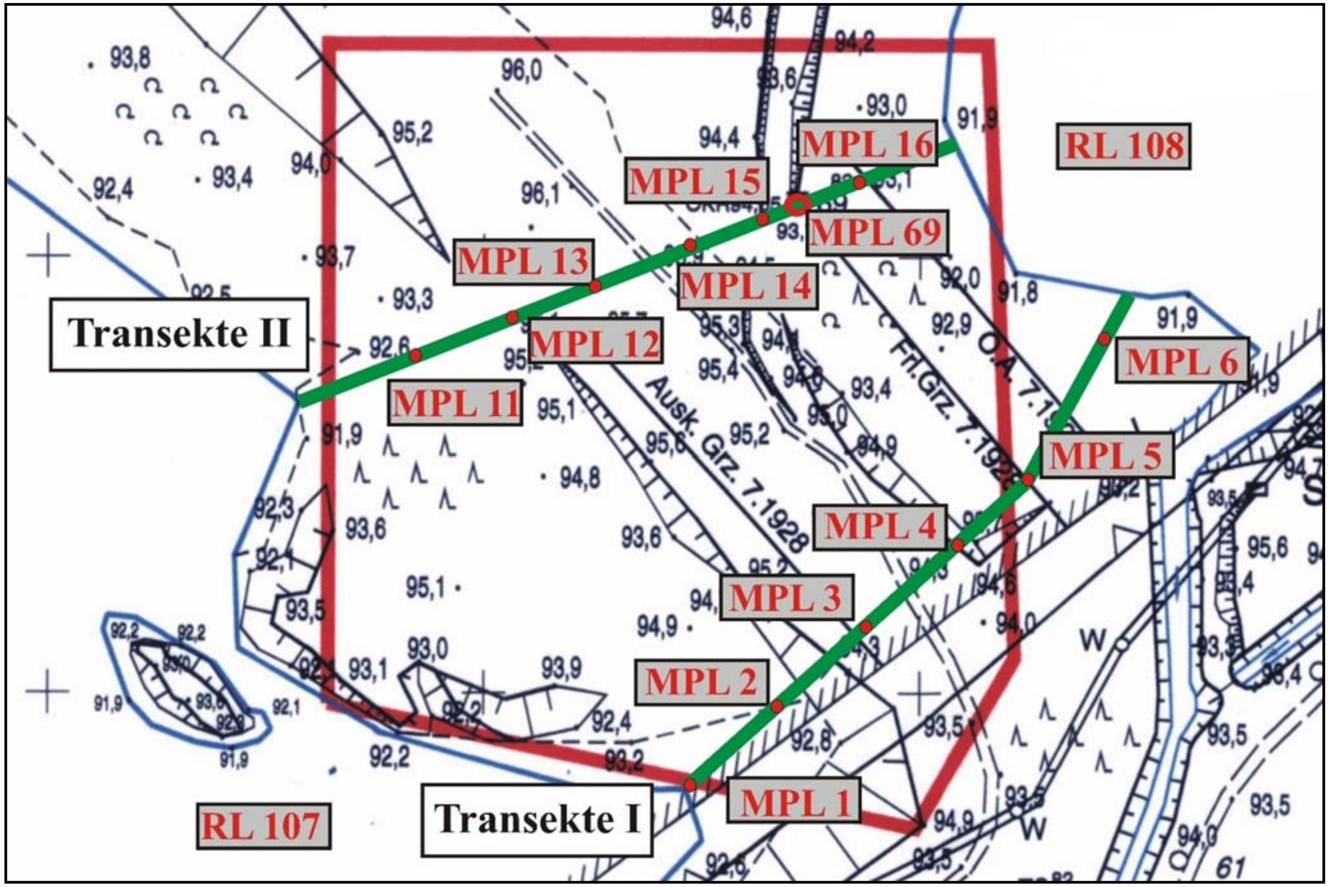
➢Tertiary C_{org} – Batchtest Plessa-Sediment (Fungi, hSRB)

„DOC-supply" by autochthonic biocenosis



⇒ **High concentrations of dissolved organic substances, strong discolouring of the solution**

➢ Sulphate reduction - old dump Plessa



Transekte II

- dump-GW

Transekte I

- Influenced by lake-water
- Margin structure

Investigation site

- Dumped before ca. 80 years

Dump Plessa – hydrogeochemical situation

Mining lakes:

pH-Wert 2,4

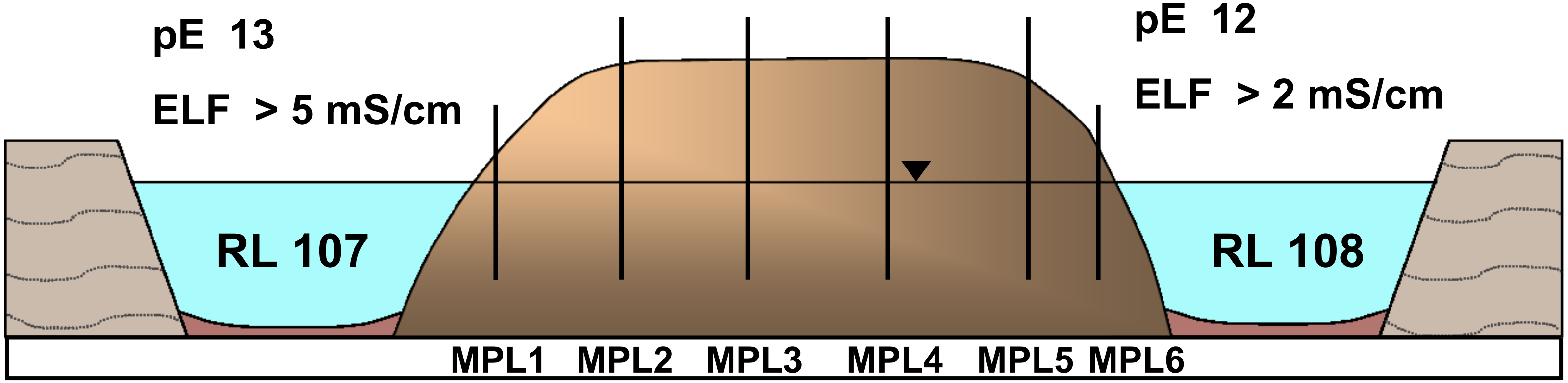
pE 13

ELF > 5 mS/cm

pH-Wert 3

pE 12

ELF > 2 mS/cm



Dump body:

Transekte I

pH-Werte 2,7 - 4,8

pE 5 - 9

ELF > 1 - 3 mS/cm

Transekte II

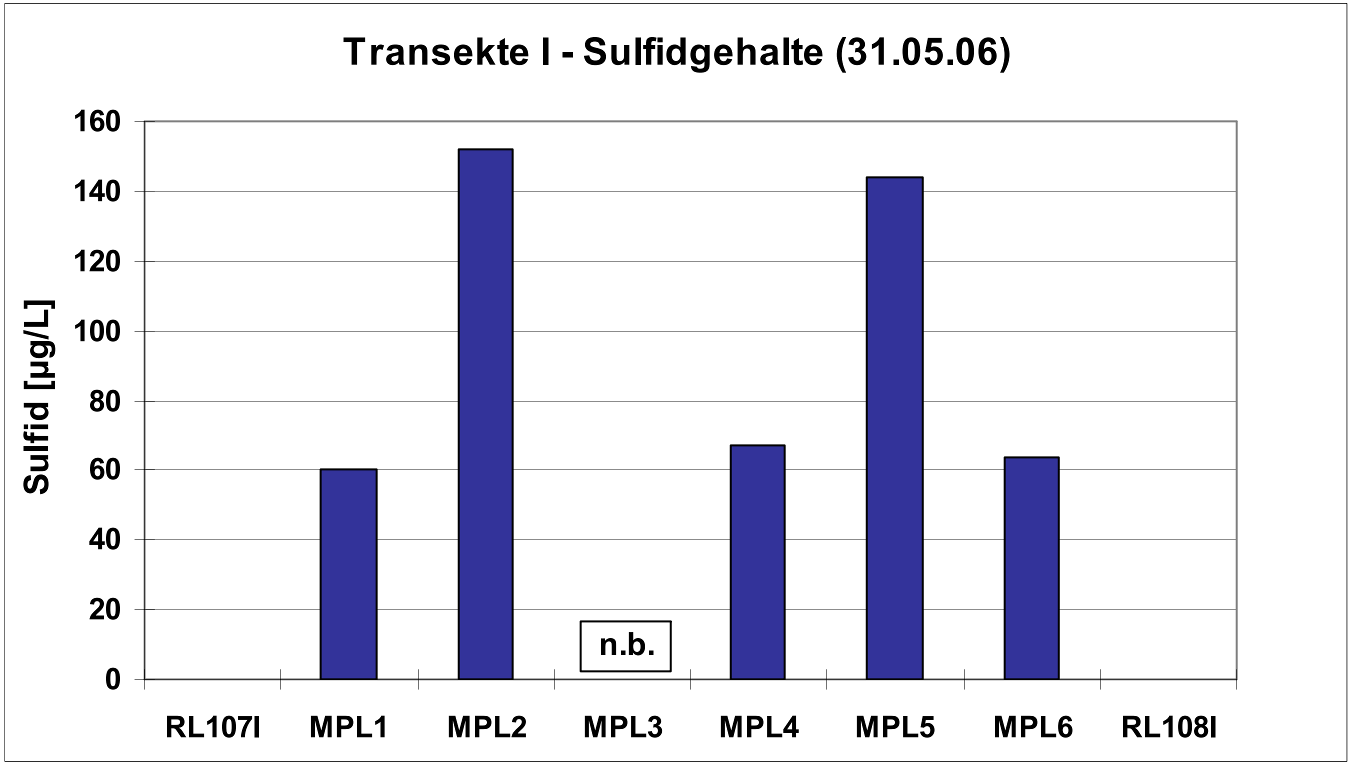
pH-Werte 3,5 - 5

pE 2 - 6

ELF > 1 - 3 mS/cm

	RL 107	*RL 108*	*Dump Body*
Sulphat [mg/L]	3500	500	650 - 1500
Iron [mg/L]	700	50	200 - 500

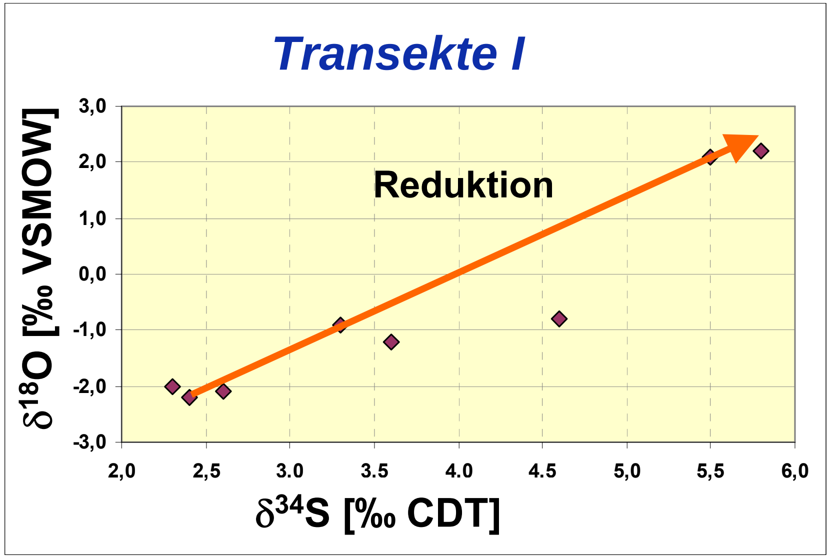
➢ Dump Plessa – sulphide evidence

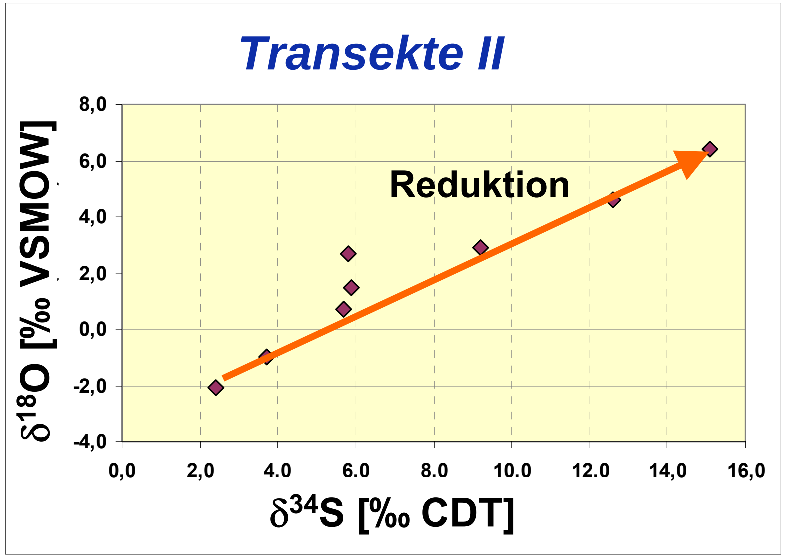


- ➢ Evidence of sulphide at all water gauges
- ➢ Sulphate reduction is also relevant by pH-values < 5 !

➢ Dump Plessa – sulphate reduction

Isotopic values of the dissolved Sulphates: $\delta^{18}O$ and $\delta^{34}S$





➢ **positive correlation between $\delta^{18}O$- und $\delta^{34}S$-values**

➢ Dump Plessa – sulphate reduction

Comparison of S-isotope signatures of co-existing reduced and oxidised anorganic sulphur within the sediment

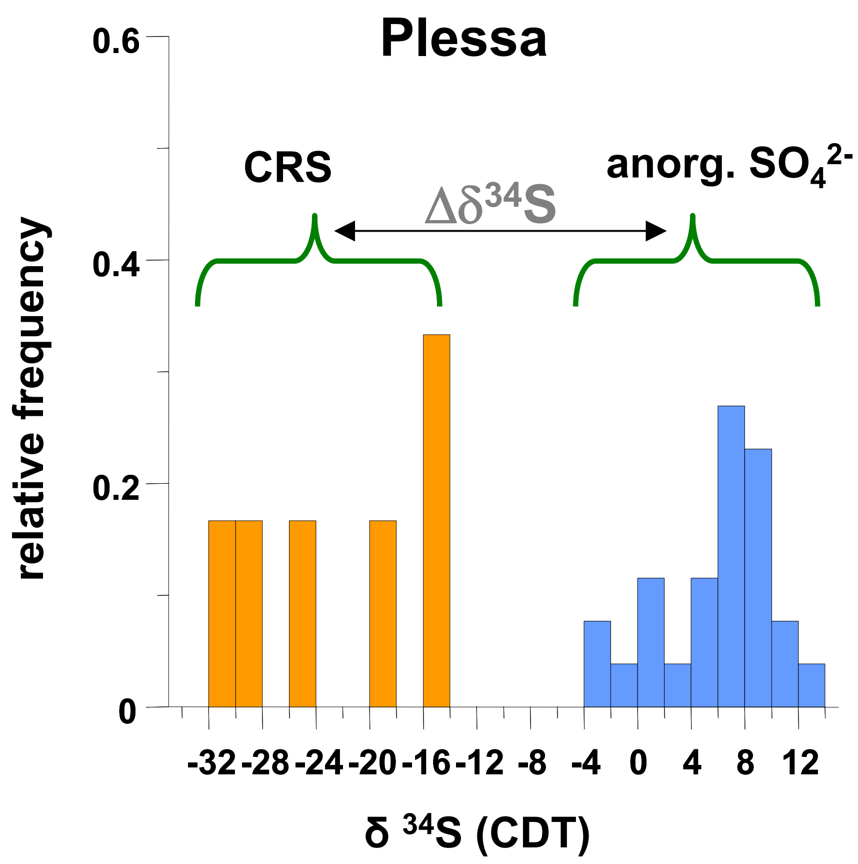
~~δ^{34}S-CRS = δ^{34}S-SO_4-sed~~

~~oxidation-dominated~~

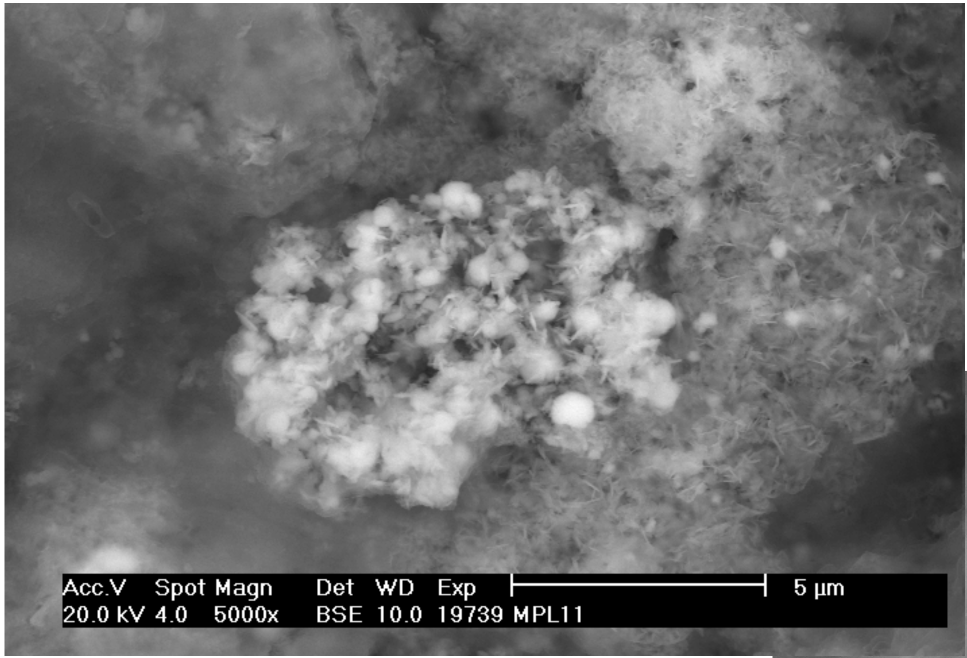
δ^{34}S-CRS << δ^{34}S-SO_4-sed

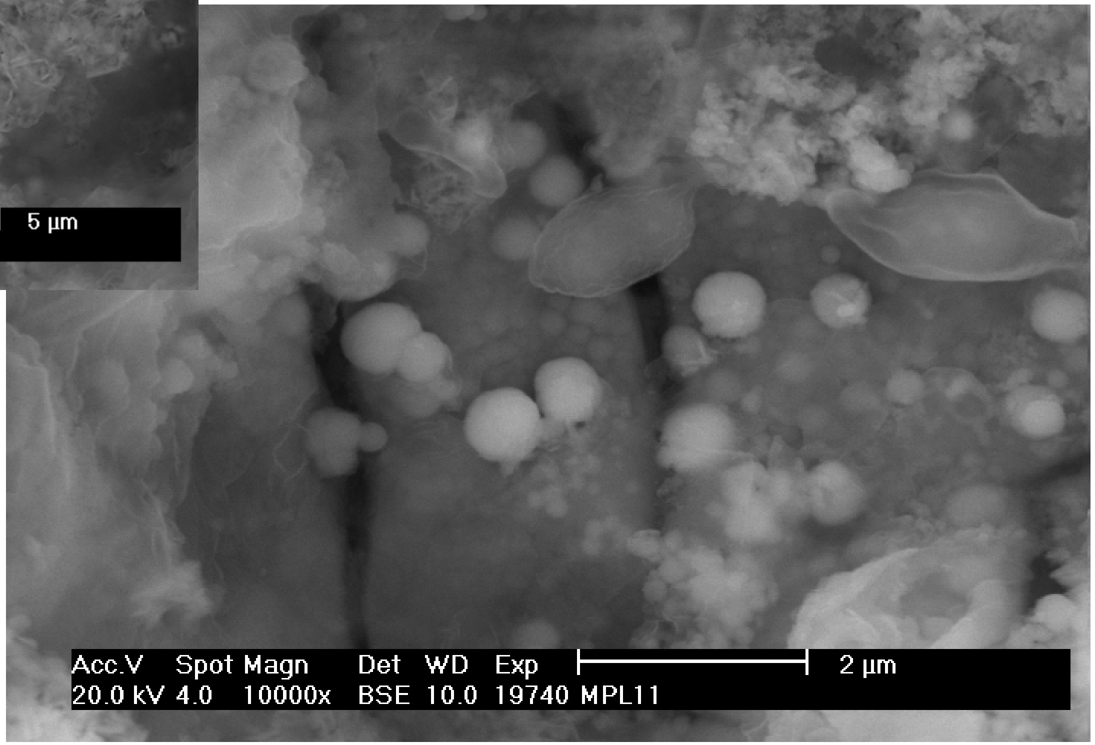
↓

reduction-dominated

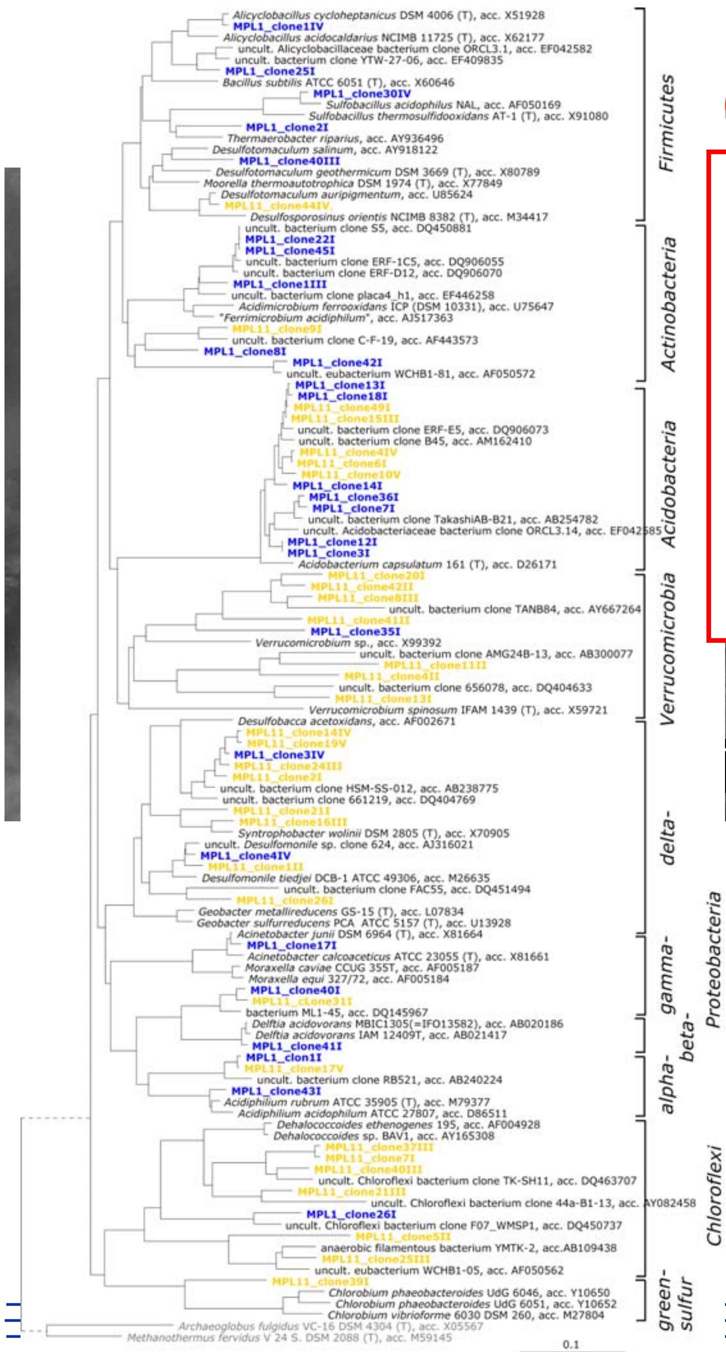


➢ Dump Plessa – autochthonic microorganisms





chthonic microorganisms



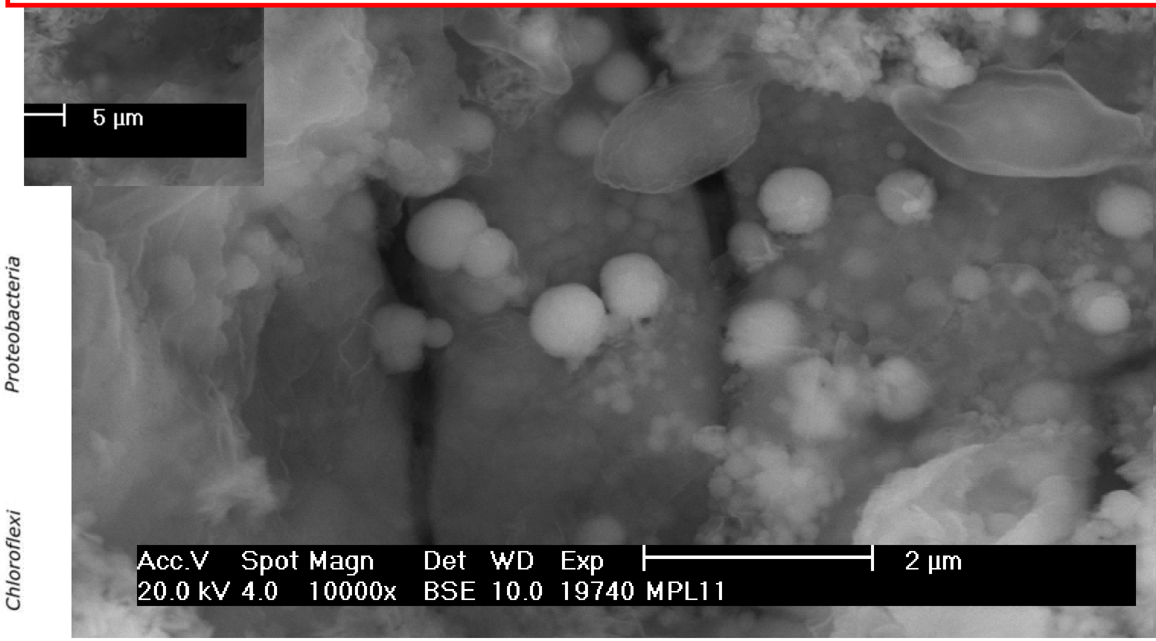
Molecular-genetic investigation

(Workinggroup Seifert/ Schlömann)

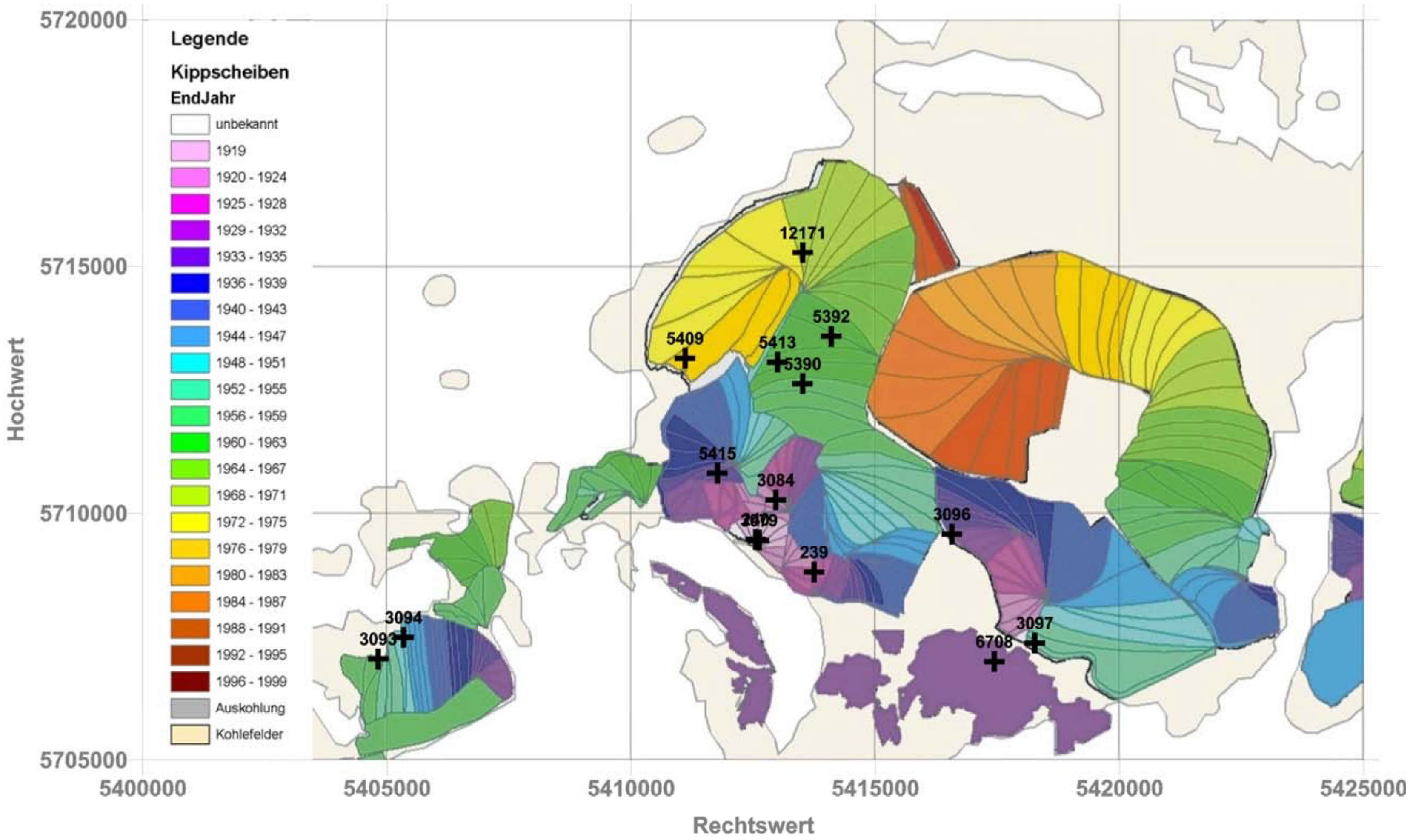
⇒Complete surprise - high diversity

⇒Acidophilic sulphate reducers

⇒Fermenting bacteria

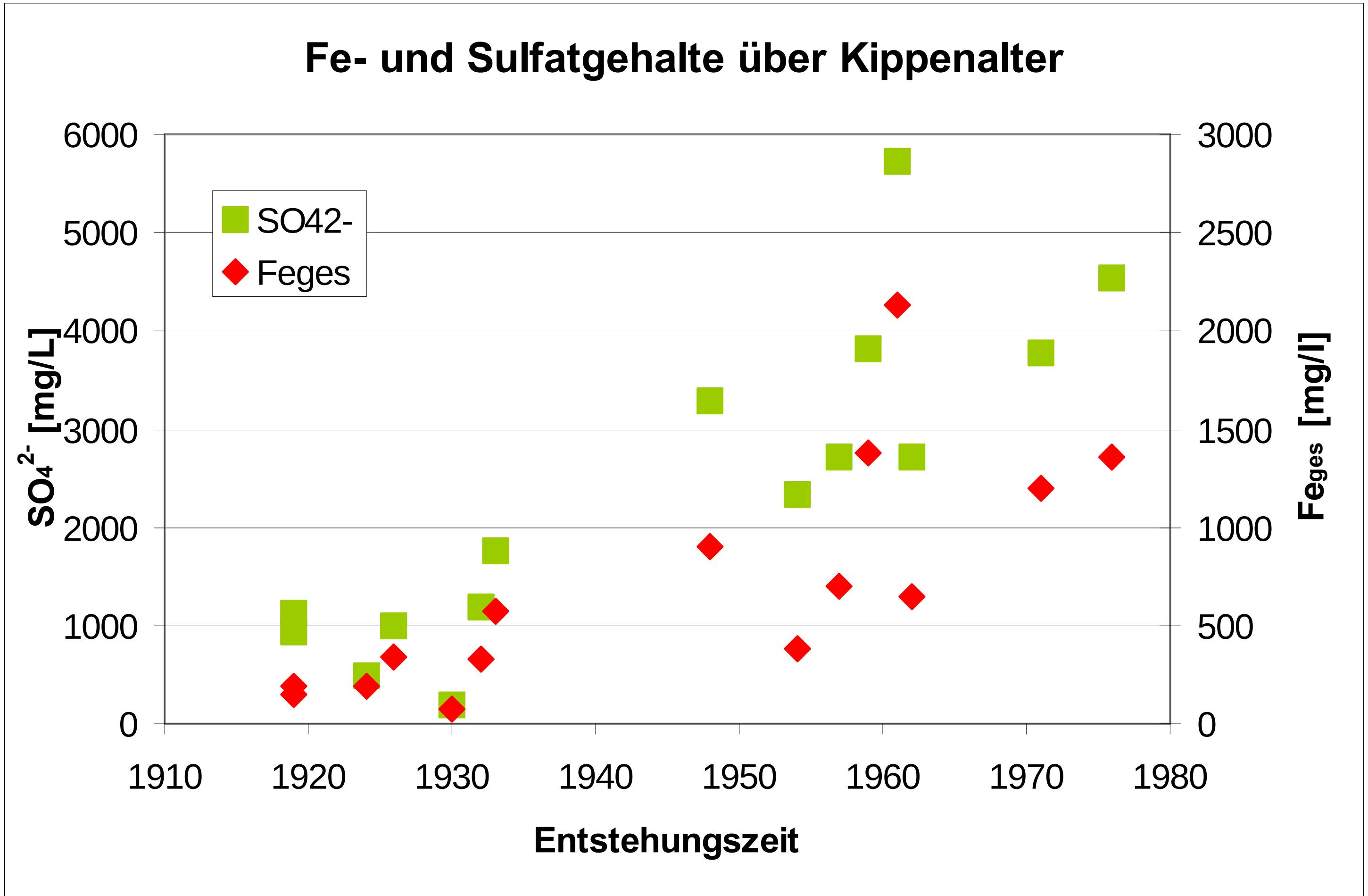


➢Spacious monitoring – messurement points (age)



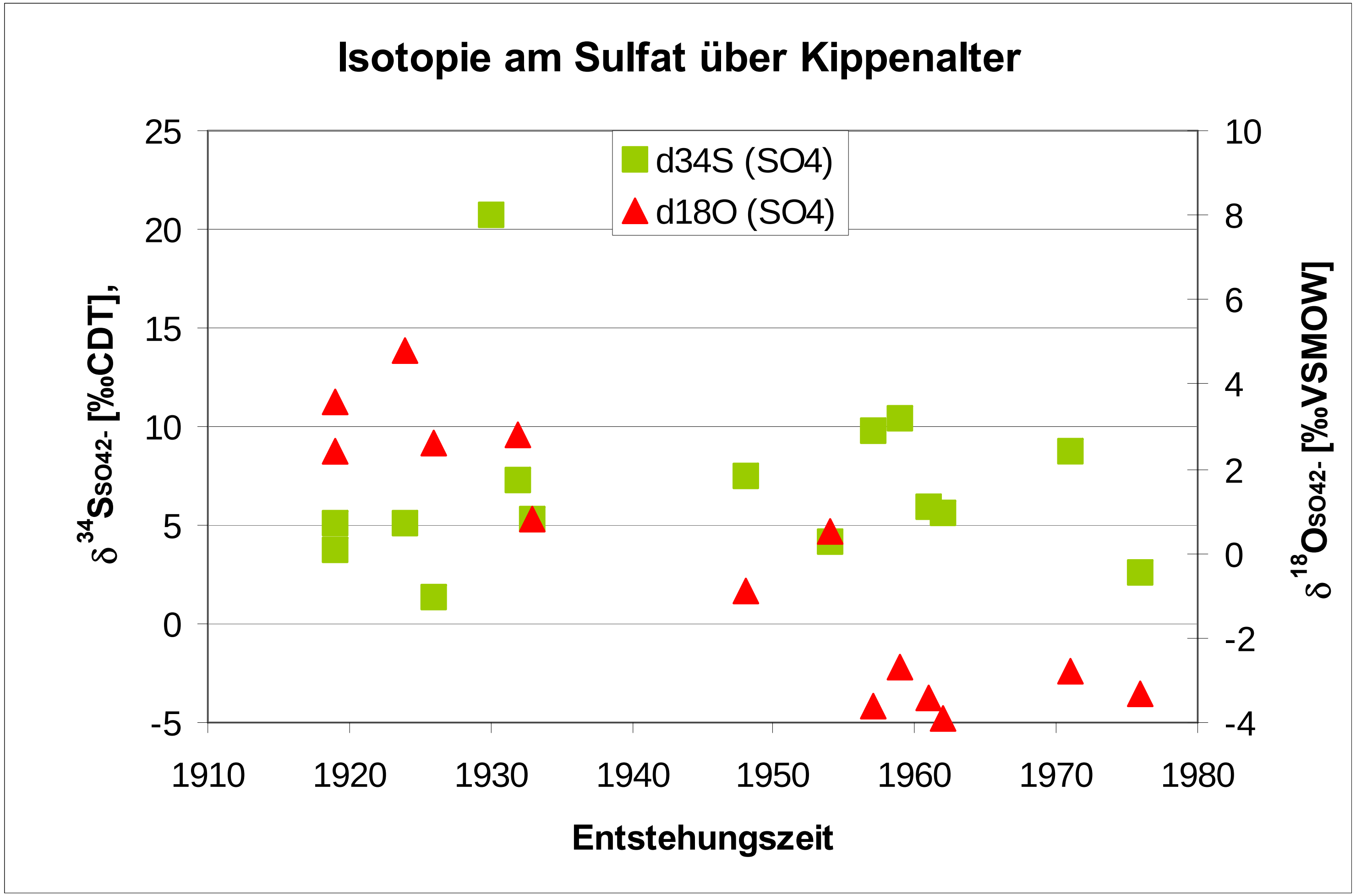
➢ Iron, sulphate content related to the age

Well correlated decrease



➢ Sulphate isotopy related to the age

^{18}O – typical sulphate reducing effect, ^{34}S – different sources



➢ Calculation methodology for $K_{B6,5}$

As objective-pH value = 6,5 was chosen

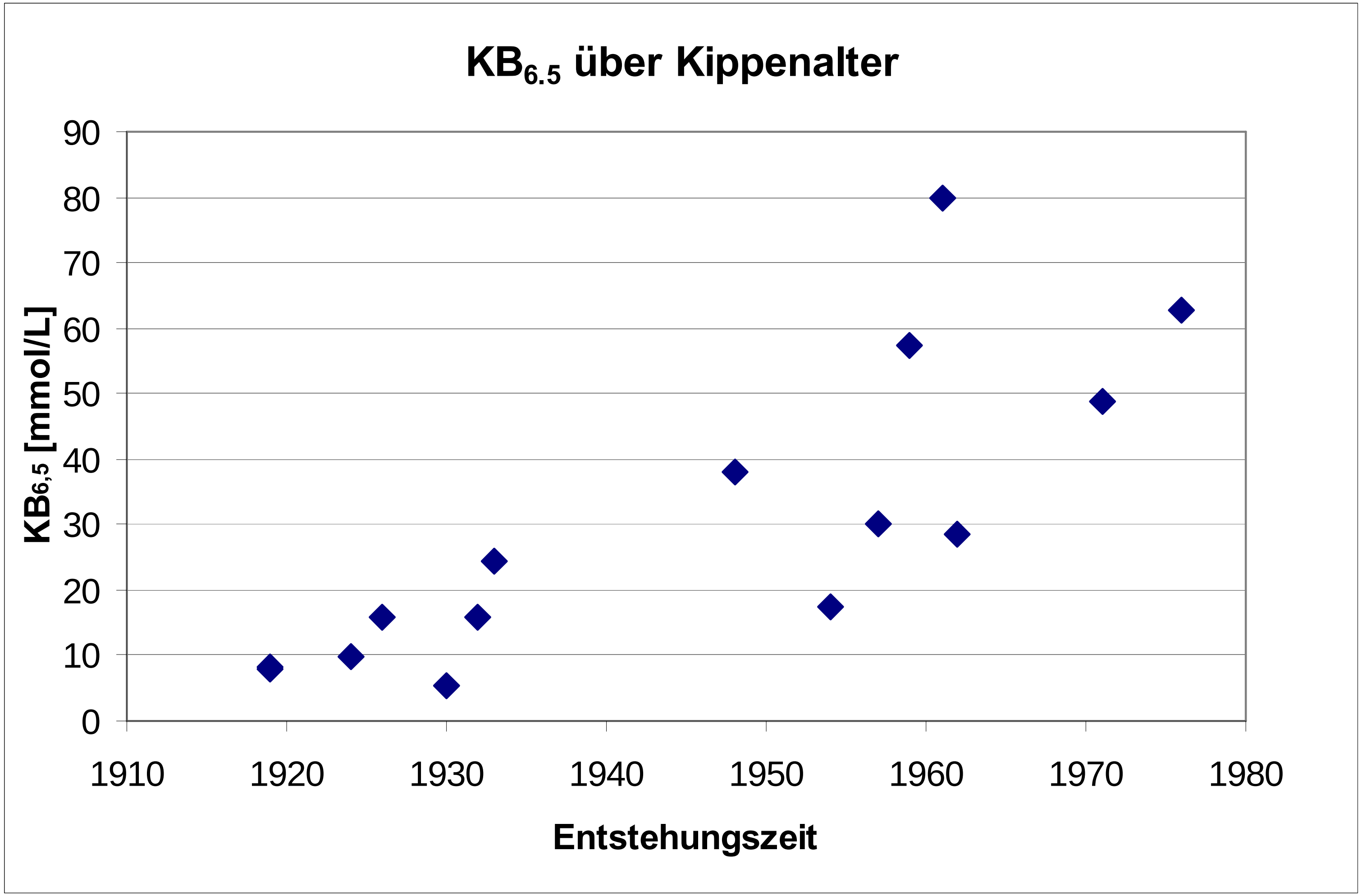
In PHREEQC – water analysis in contact in air

$Fe(OH)_{3(a)}$, $Al(OH)_{3(a)}$ can precipitate $\Rightarrow$ acid generation

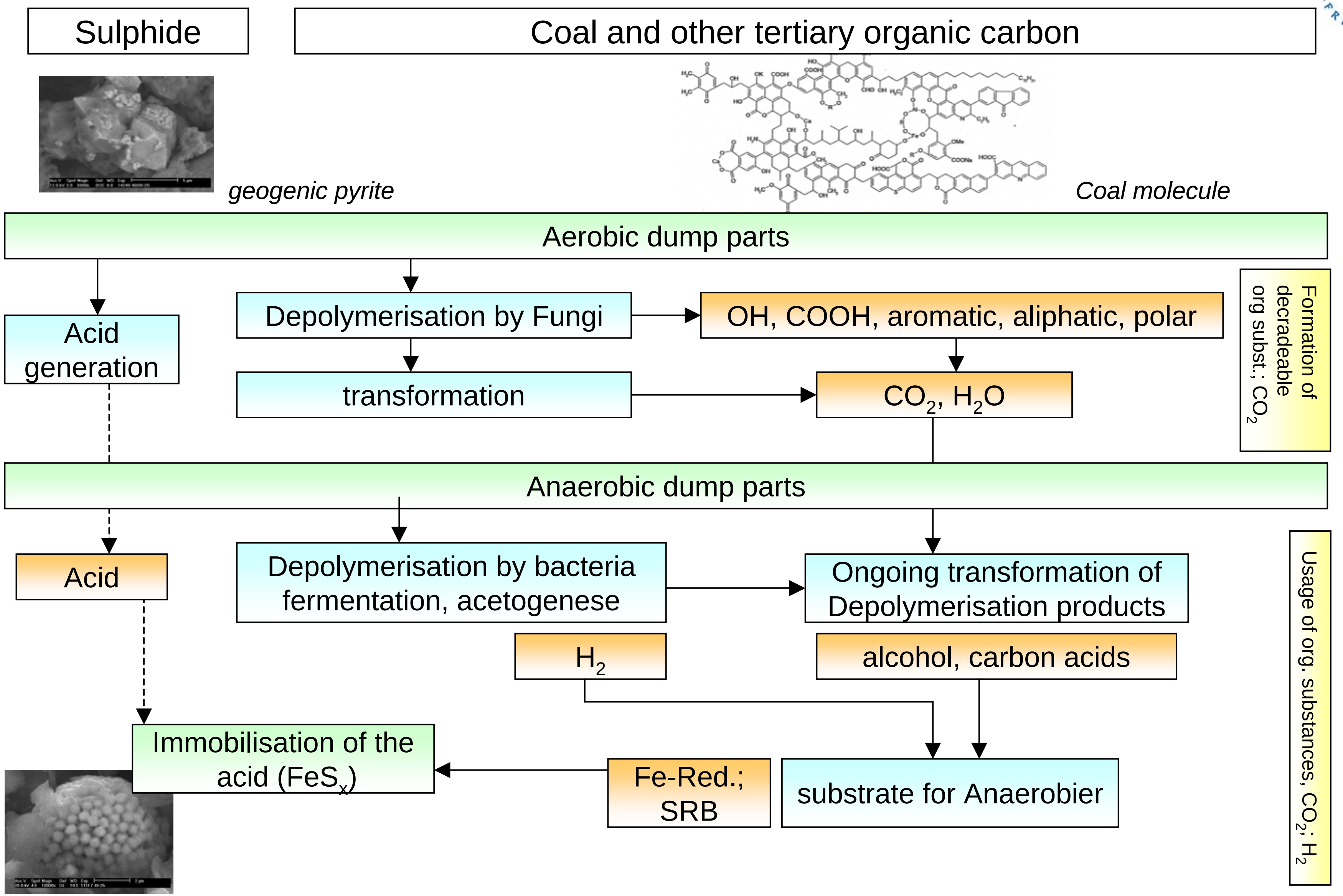
After that calculation of alkaline consumption by titration to reach pH=6,5

➢ Calculation potential acidity ($K_{B6,5}$) related to the age

Clear decrease of the values for elder dump sites!



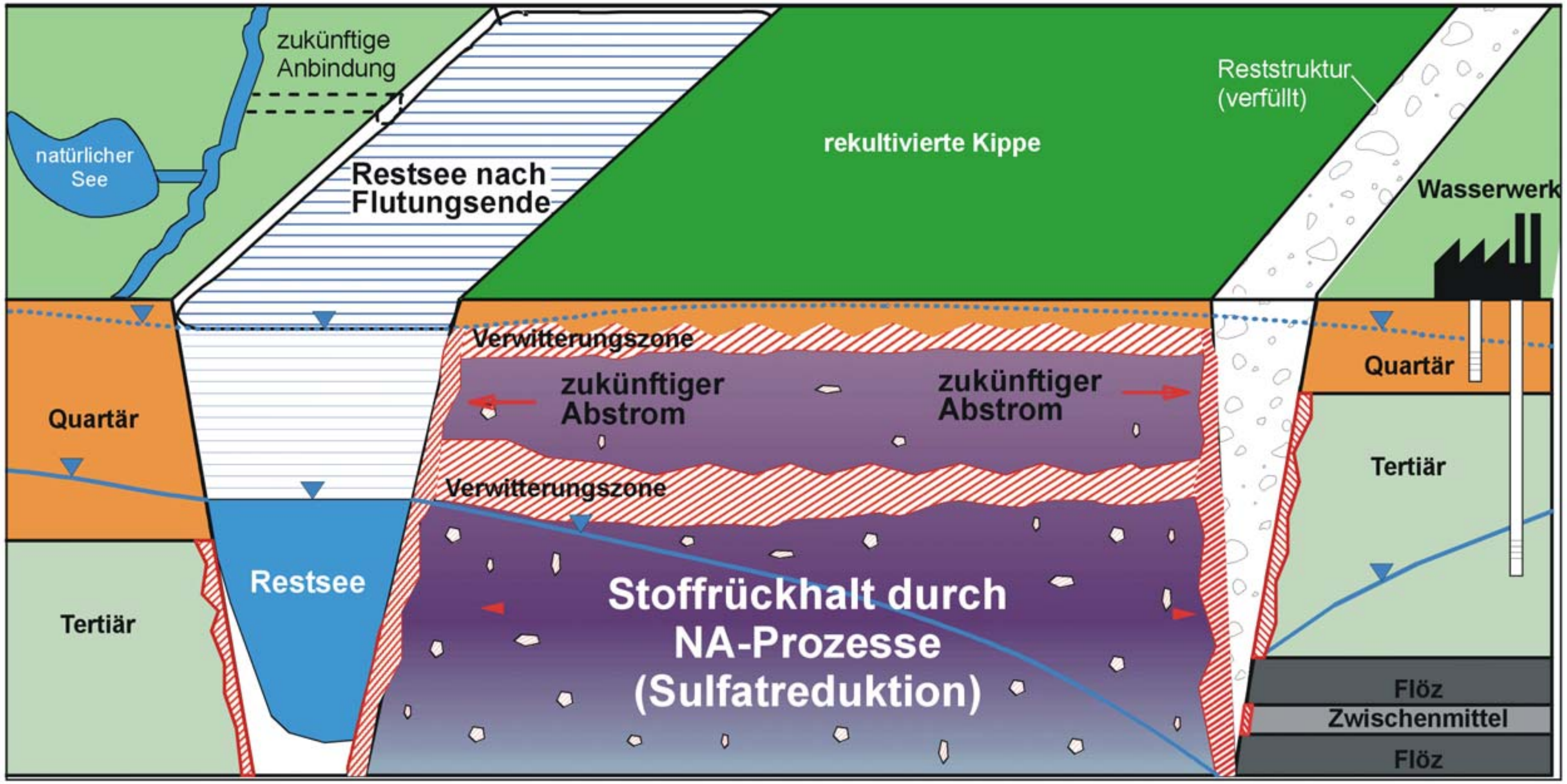
➢Model of reduction and microbial use of tertiäry C_{org}



Part C

Main results in relation to a potentially reprocessing of mining dumps and tailings

➢For Corg rich Overburden dumps



⇒ **Understanding of the weathering zones**

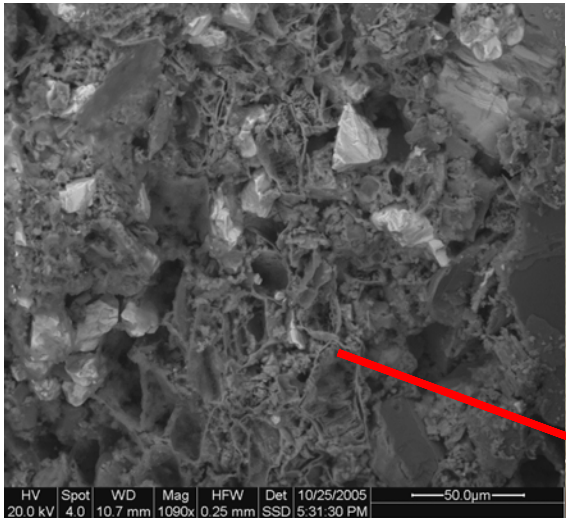
⇒ **Therein great part of the metals dissolved**

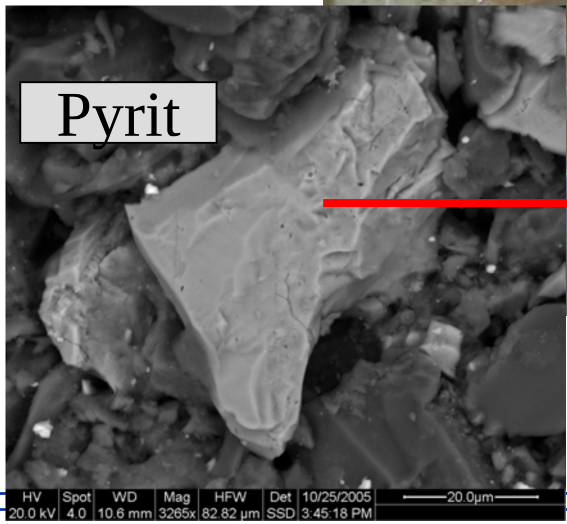
⇒ **On the interface of oxidized and reduced zones - accumulations**

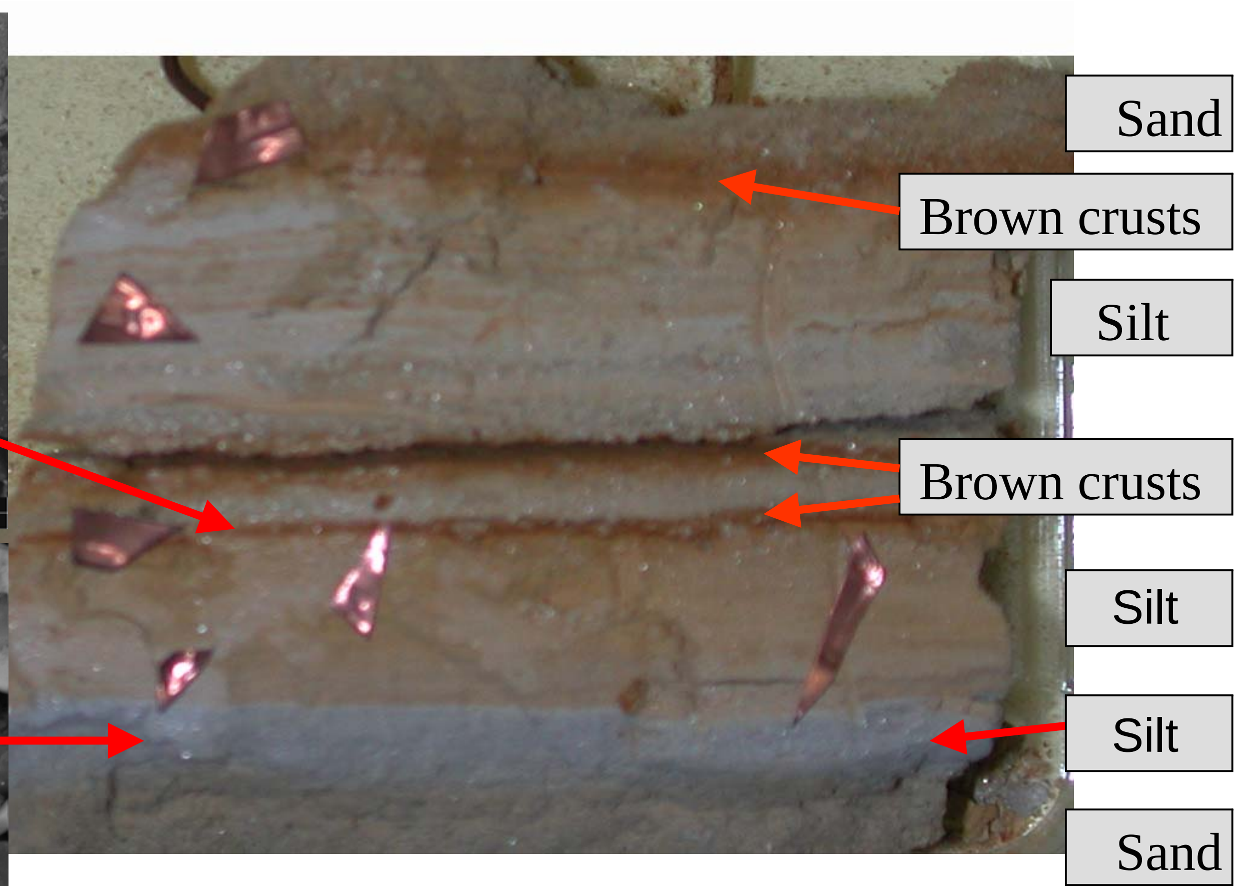
⇒ **Knowledge of dumping technology, time space of work levels etc.**

➢Crusts in ore mining heaps/ tailings

Profil A (0,6 – 0,63 m)



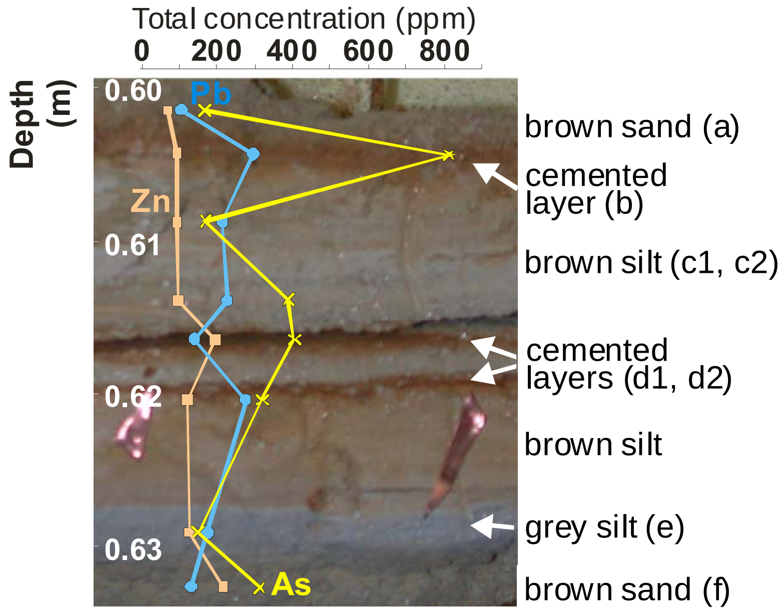




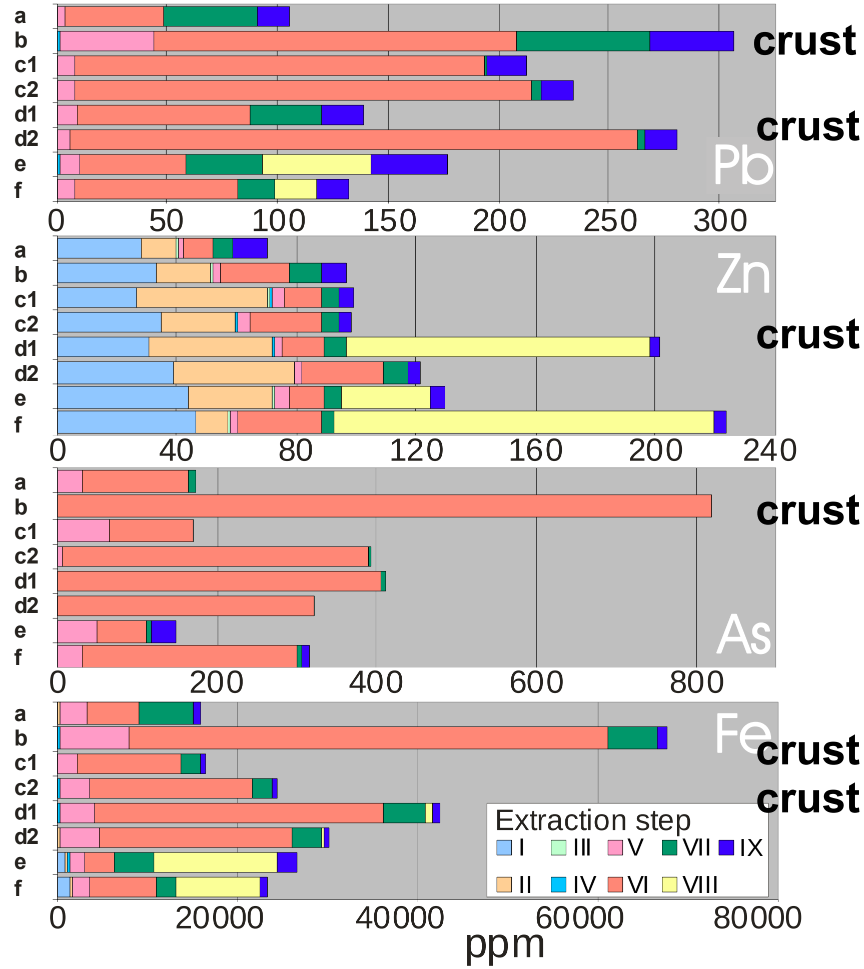
Oxidation fronts and crusts in fine grained materials

➢Ore mining heaps/ tailings – sequential extraction

A. Teilbereich von Profil A (0.60-0.63 m)



B. Freigesetzte Kontaminanten bei der Extraktion der Lagen aus Abb. A



Steps of extraction:

I – Water soluble fraction Zn
II – Ionic exchangeable fraction Zn
III – Carbonatic fraction
IV – Easy reduceable fraction
V – Organic fraction
VI – Fe(III)-Oxihydroxid- fraction ±Jarosit As, Pb
VII – Crystalline Fe(III)-minerals (z.B. Jarosit) Pb
VIII – To oxidise fraction (Sulphides) Pb, Zn
IX – Residual fraction (silicates)

Conclusions

➢Conclusions

⇒ Natural attenuation processes in mining dumps/ tailings are relevant in an long-term view

⇒ C_{org}-rich overburden dumps – sulphate reduction by autochthonic bacteria – high rates possible – enhancing technologies

⇒ Process engine – depolymerisation of TOC

⇒ Sulphate reduction also shown for pH-values < 5

⇒ Ore mining heaps and tailings – crust formation at capillary fringes – hydraulic encapsulation of heap parts

⇒ Importance of silica rich gel layers – metal enrichment

⇒ Understanding of the (hydro)geochemical reorganisation processes important for flushing prognosis

⇒ …. also very important if reprocessing of dumps/ heaps / tailings are in mind

Thank you for your attention