UNIVERSITÄT BAYREUTH

BayCEER
Bayreuth Center of Ecology and Environmental Research

When hydrology meets chemistry - Insights into the coupling between transport and reaction

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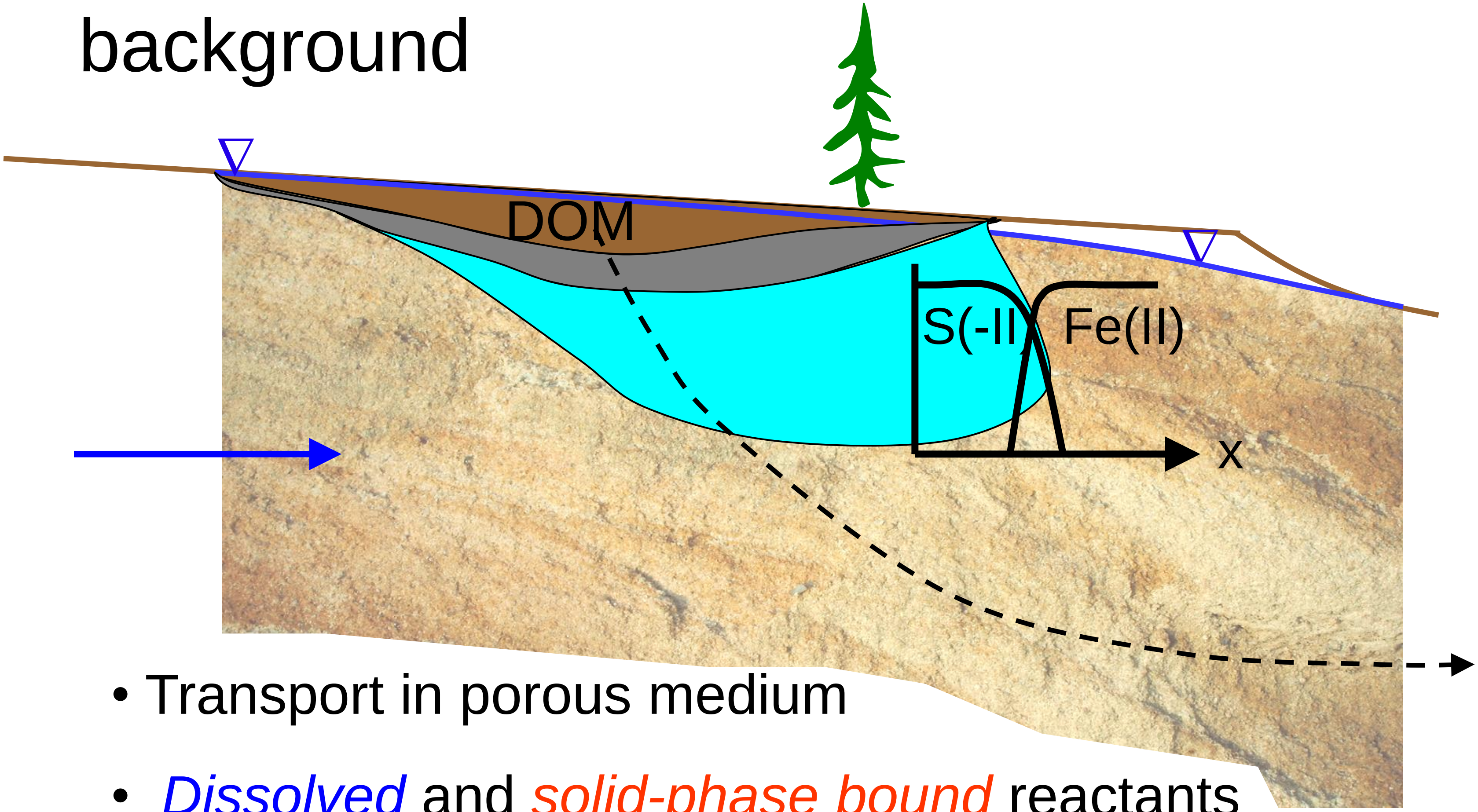
background



- Transport in porous medium
- *Dissolved* and *solid-phase bound* reactants

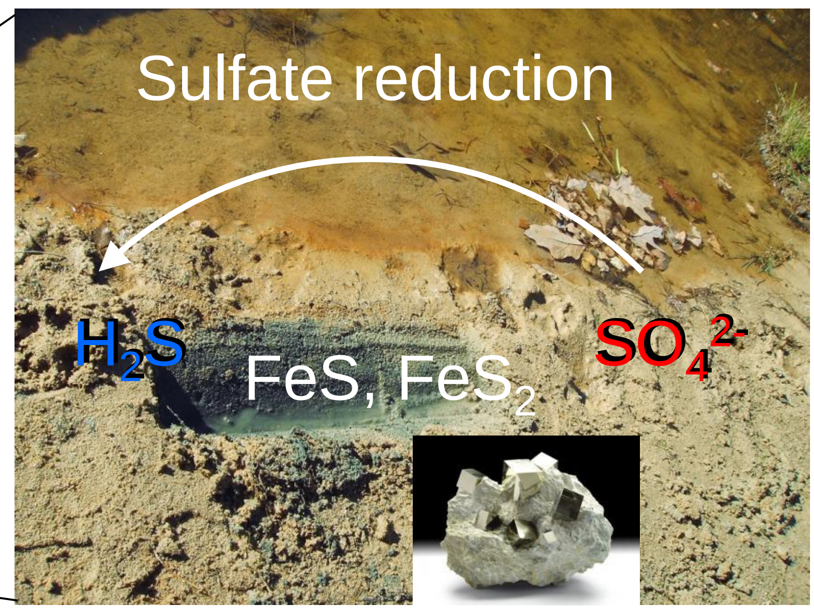
Is there an effect of flow on reaction rate and turnover?

Outline

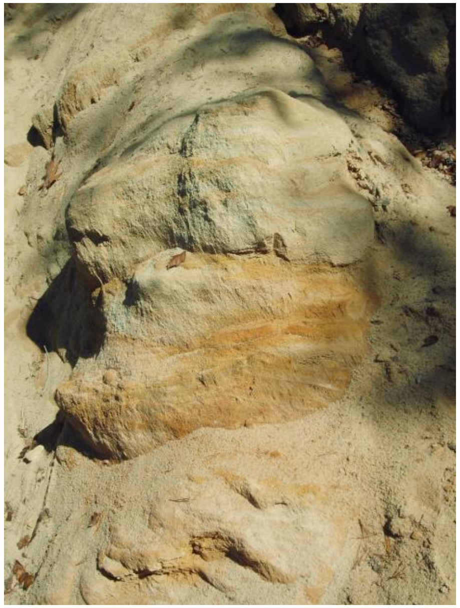
1. The geochemical frame work: Pyrite formation
2. Transport control of geochemical reactions
3. The Damköhler number – a usefool tool?

1) The geochemical frame work: Pyrite formation

- nutrients, contaminants
- C and electron cycling

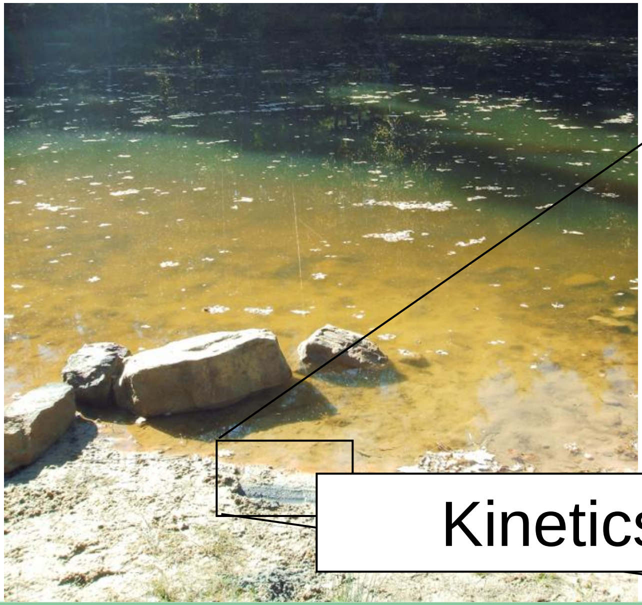


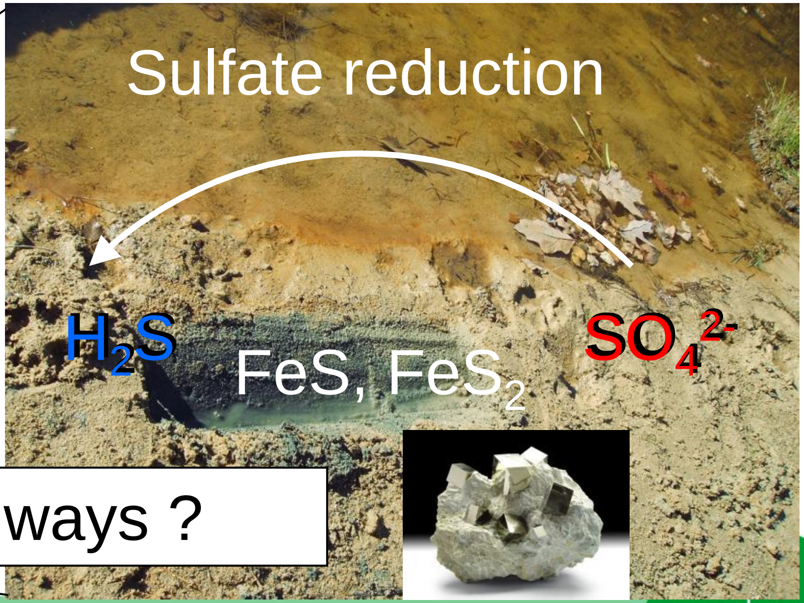
1) The geochemical frame work: Pyrite formation



$$2\ FeOOH + 3\ H_2S \rightarrow 2\ FeS + S° + 4\ H_2O$$

$$FeS + S° \rightarrow FeS_2$$





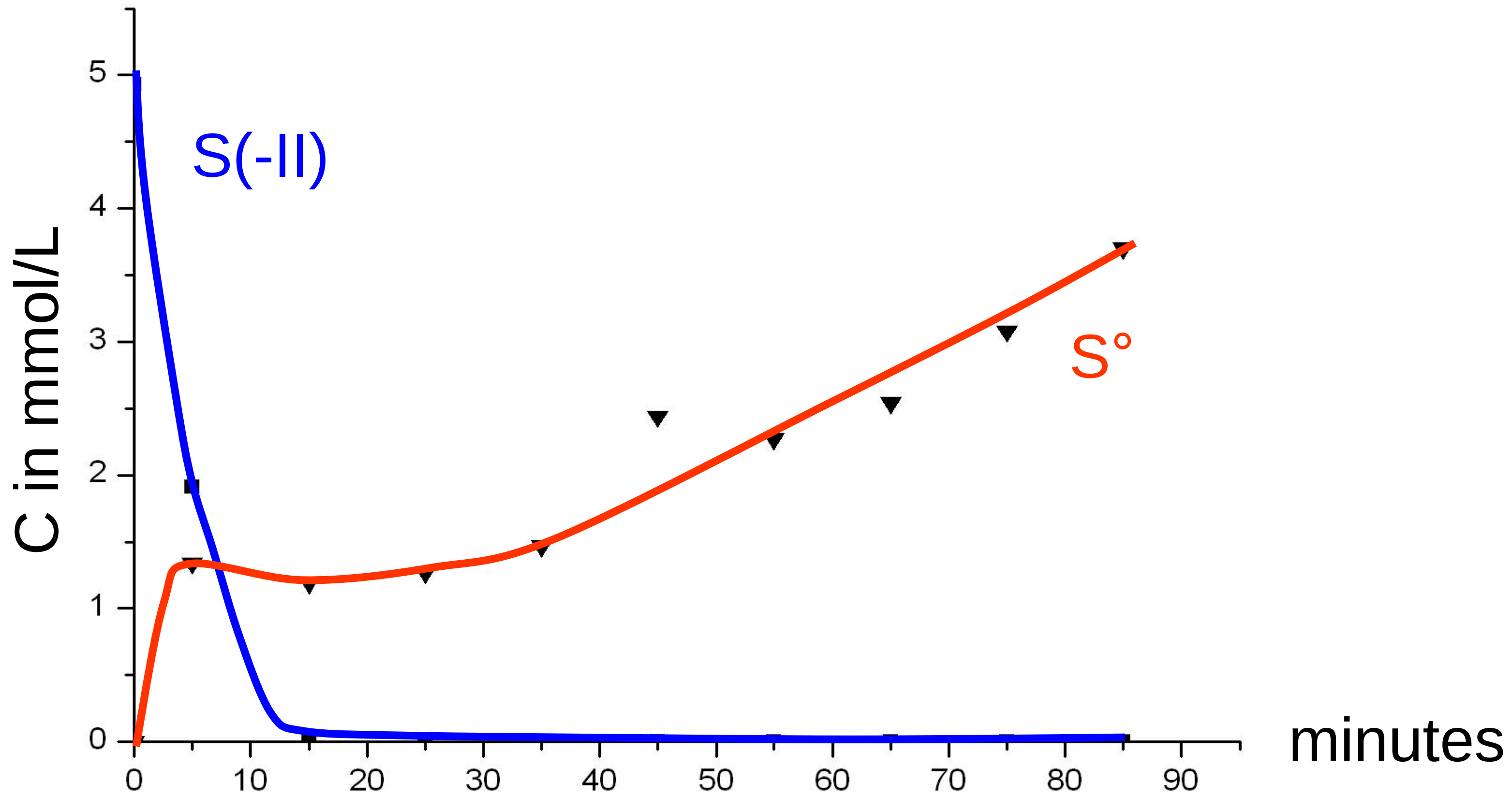
Kinetics, pathways ?

„Long time“ Batch Experiments

- 5 mmol S(-II) + 25 mmol/L Lepidocrocite
- Glove Box
- pH 7

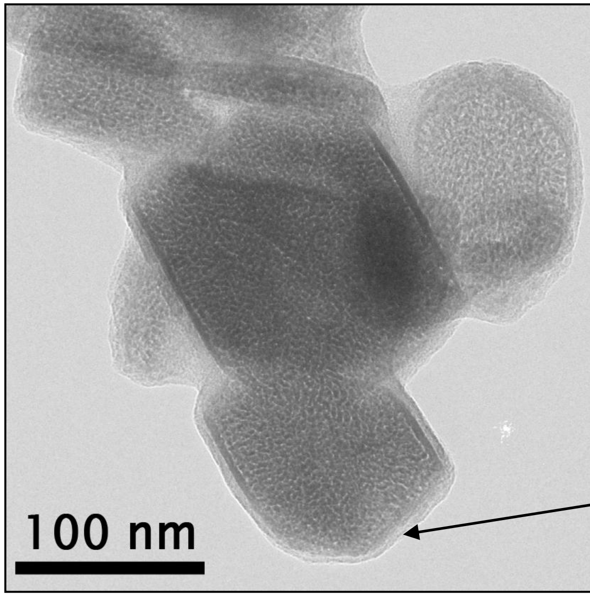
2 h 2 weeks

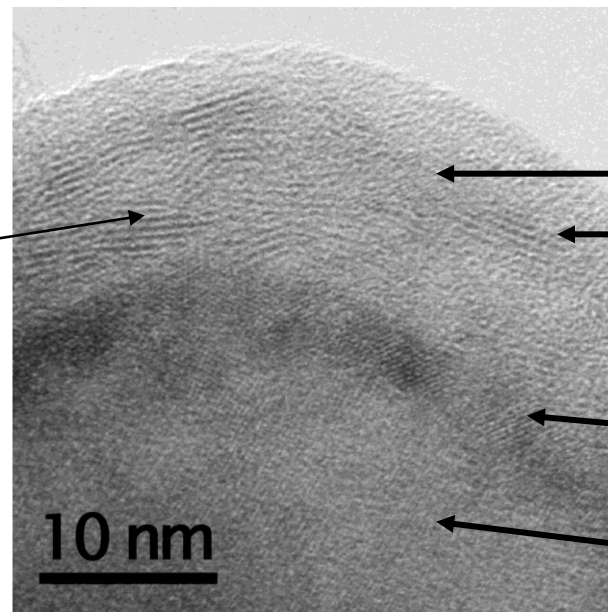
Dissolved Sulfide is consumed after 15 minutes



Formation of a FeS-layer on the lepidocrocite surface after 2 h

Mackinawite = FeS



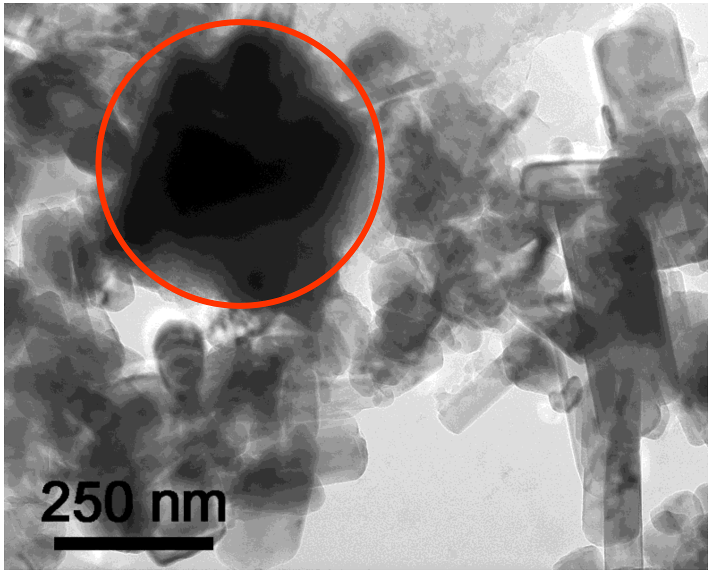


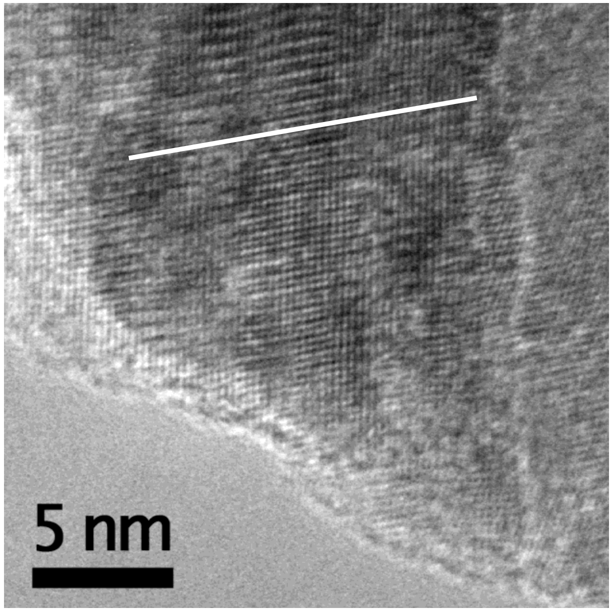
d = 2.3 Å (001)
d = 5.2 Å (111)
Mackinawite

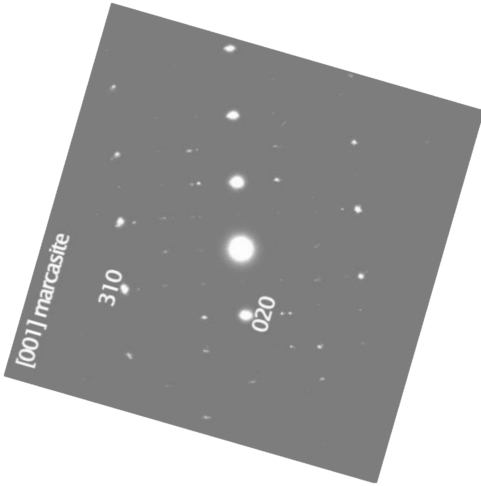
d = 2.96 Å
Magnetite

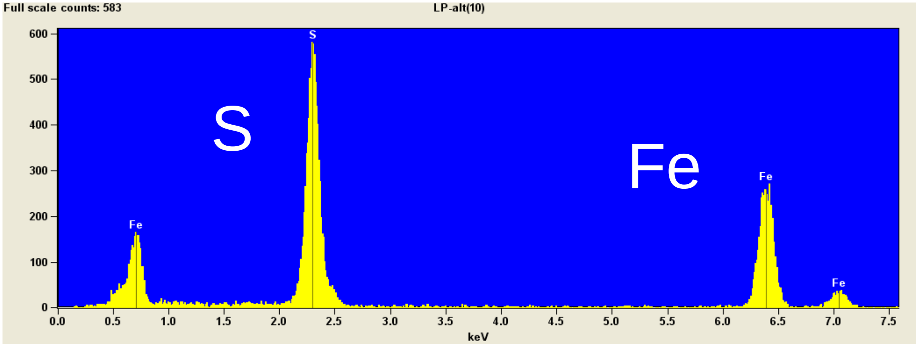
d = 3.25 Å
Lepidocrocite

After two weeks: FeS_2 formation









FeS_2 (pyrite) formation ….

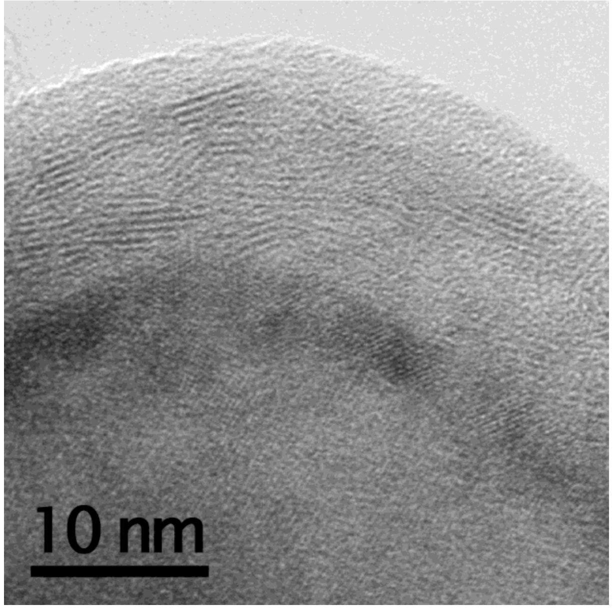
…… requires dissolved sulfur species

$FeS + S_n^{2-} \rightarrow FeS_2 + S_{n-1}^{2-}$

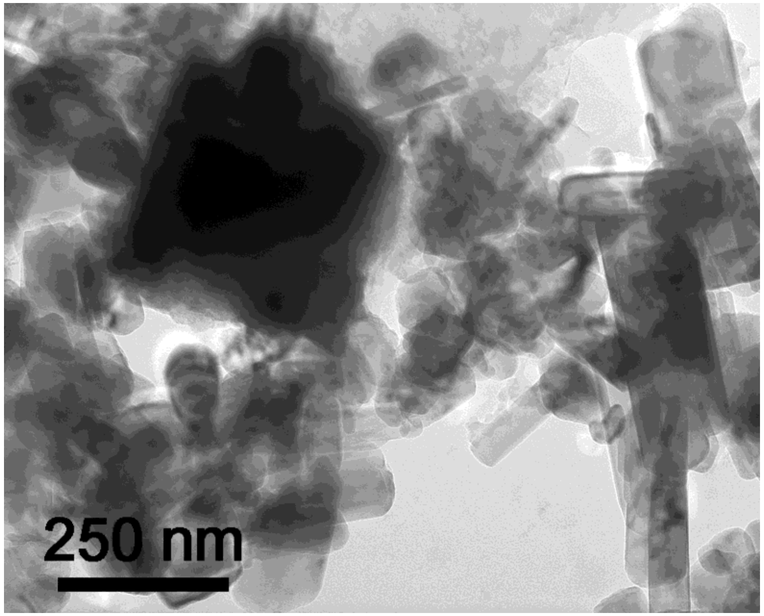
S_n^{2-}, S_{n-1}^{2-}: Polysulphides

Rickards et al, 1995, ACS Symp. Ser. 612

From the oxide surface to a new mineral



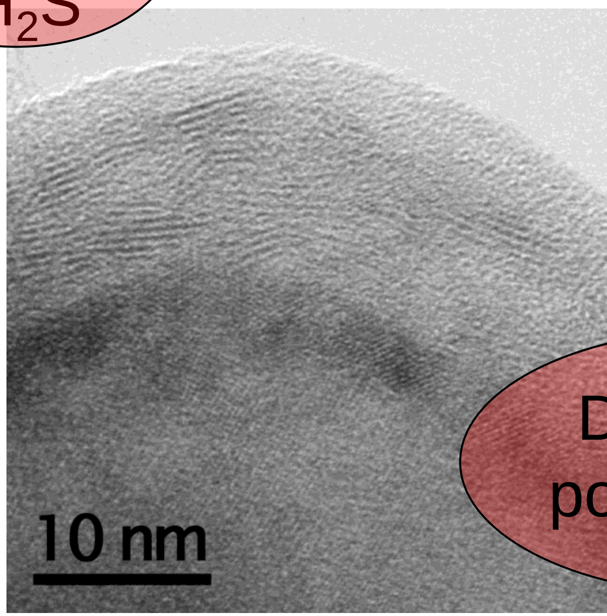
Surface
bound FeS



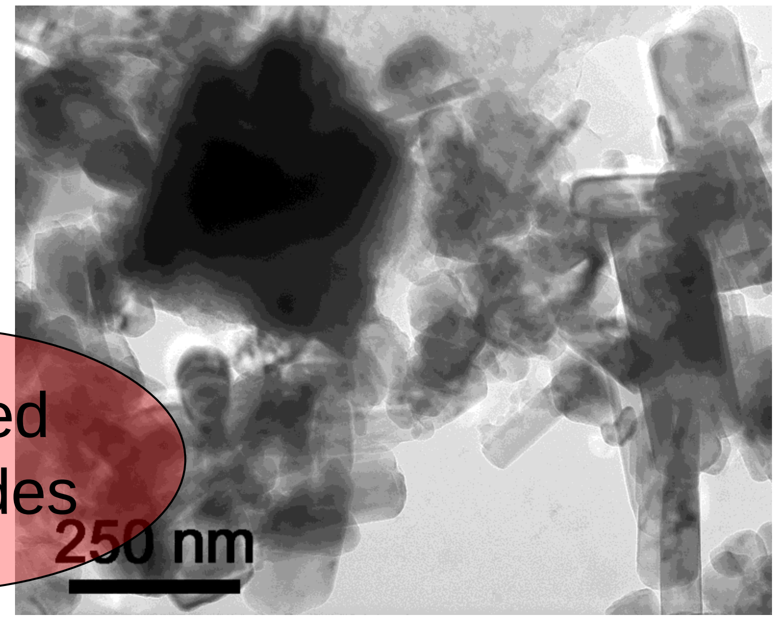
Precipitation of
a new phase

From the oxide surface to a new mineral

Dissolved H_2S



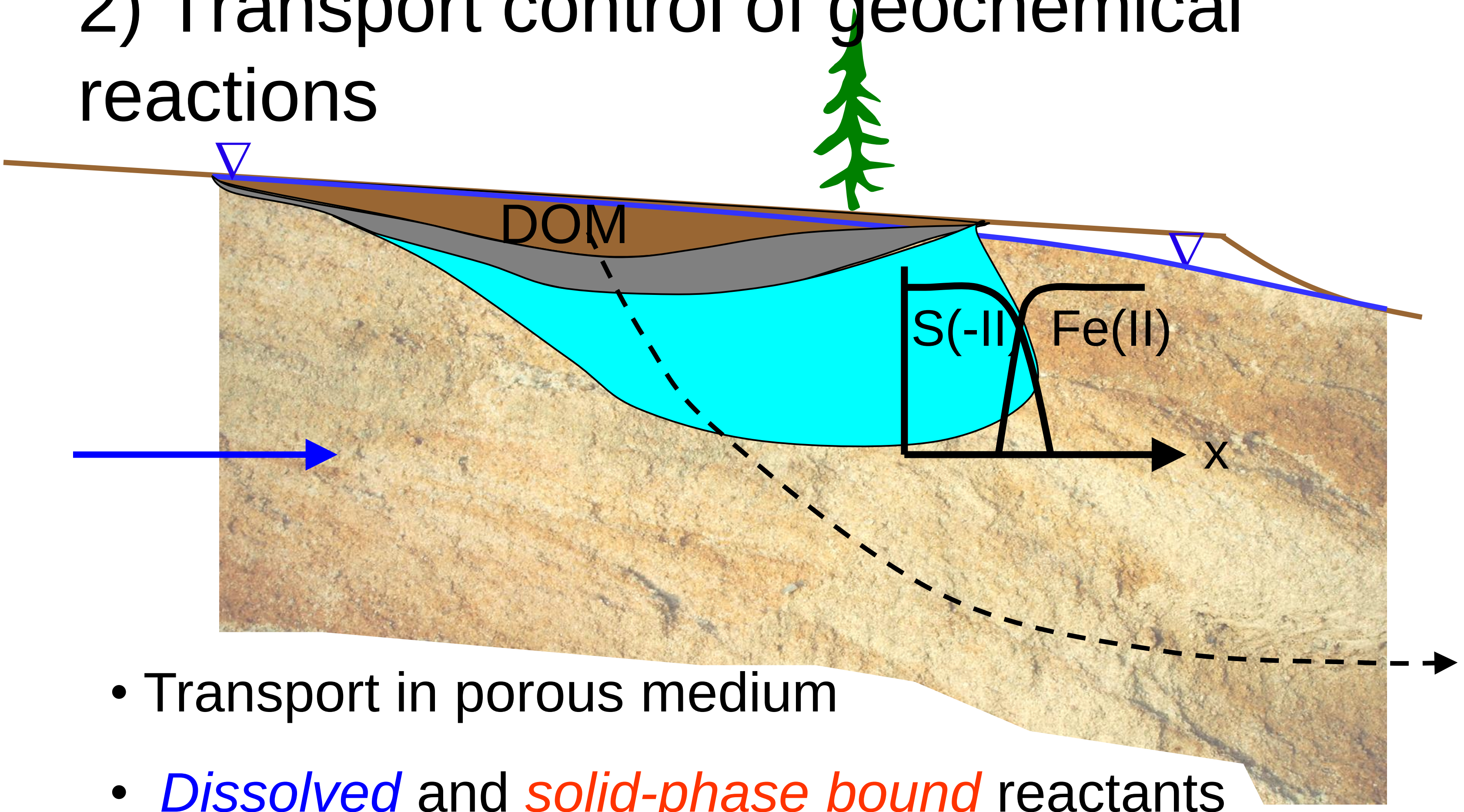
Dissolved polysulfides



Surface bound FeS

Precipitation of a new phase

2) Transport control of geochemical reactions



- Transport in porous medium
- *Dissolved* and *solid-phase bound* reactants

Is there an effect of flow on reaction rate and turnover?

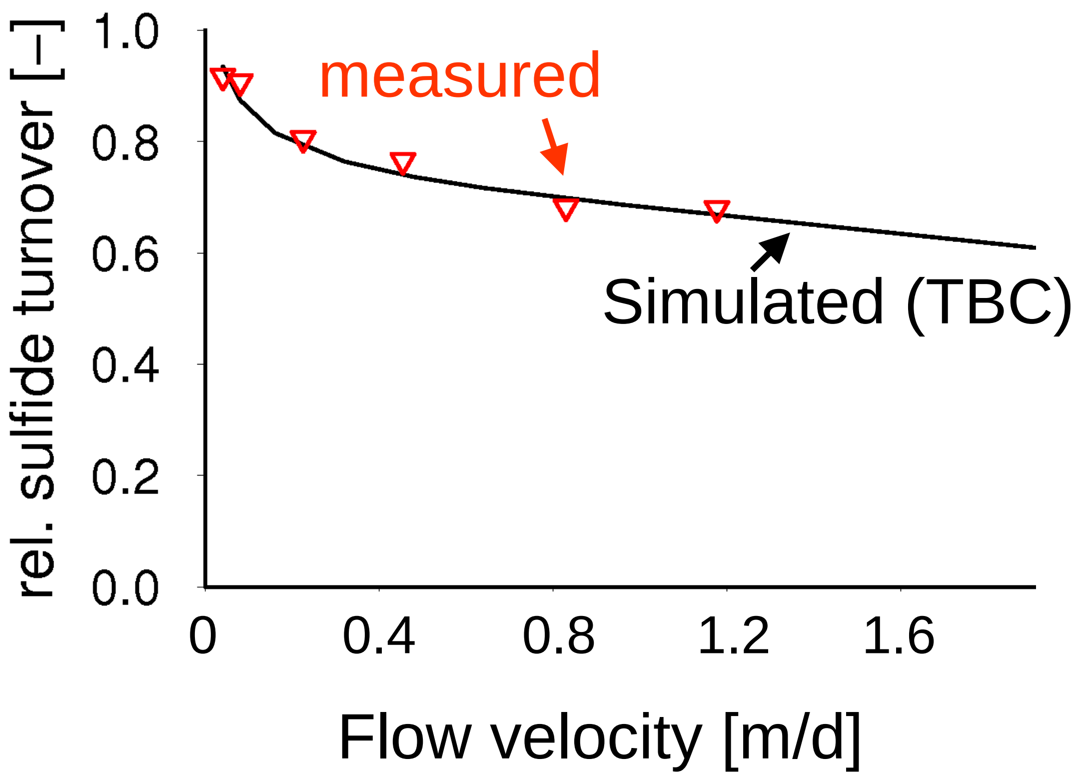
Sulfide oxidation rate is proportional to concentration of reactive surface complex

$$>FeOH_2^+ + HS^- \leftrightarrow >FeSH + H_2O$$

$$R = k \cdot \{>FeSH\}$$

Peiffer et al, ES&T, 1992 & 2007; Dos Santos Afonso et al, 1992

Sulfide turnover decreases with increasing flow rate



Transport matters !

- Penetration front of sulfide depends on flow rate
- Implications for biogeochemistry

At shorter residence time (higher flow rates) sulfide may not be competitive in regard to iron reducing bacteria (sticking to surfaces)

➔ Damköhler numbers

3) The Damköhler number – a usefool tool?

$$Da = \frac{\text{Reaction rate (mass/time)}}{\text{Transport rate (mass/time)}} = \frac{\tau}{t_r}$$

τ residence time

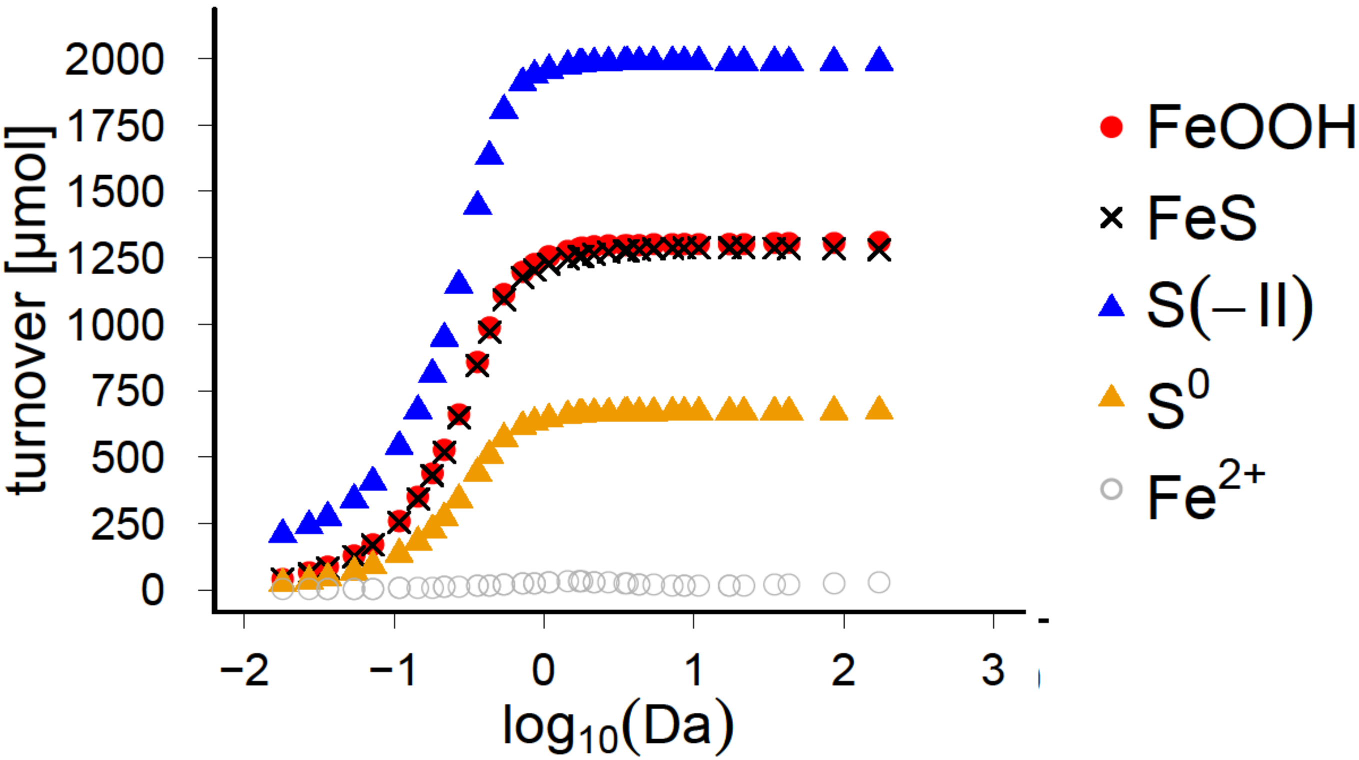
t_r characteristic reaction time (1/k)

Da > 1 reaction-dominated system

Da < 1 transport-dominated system

Turnover related to Damköhler Numbers

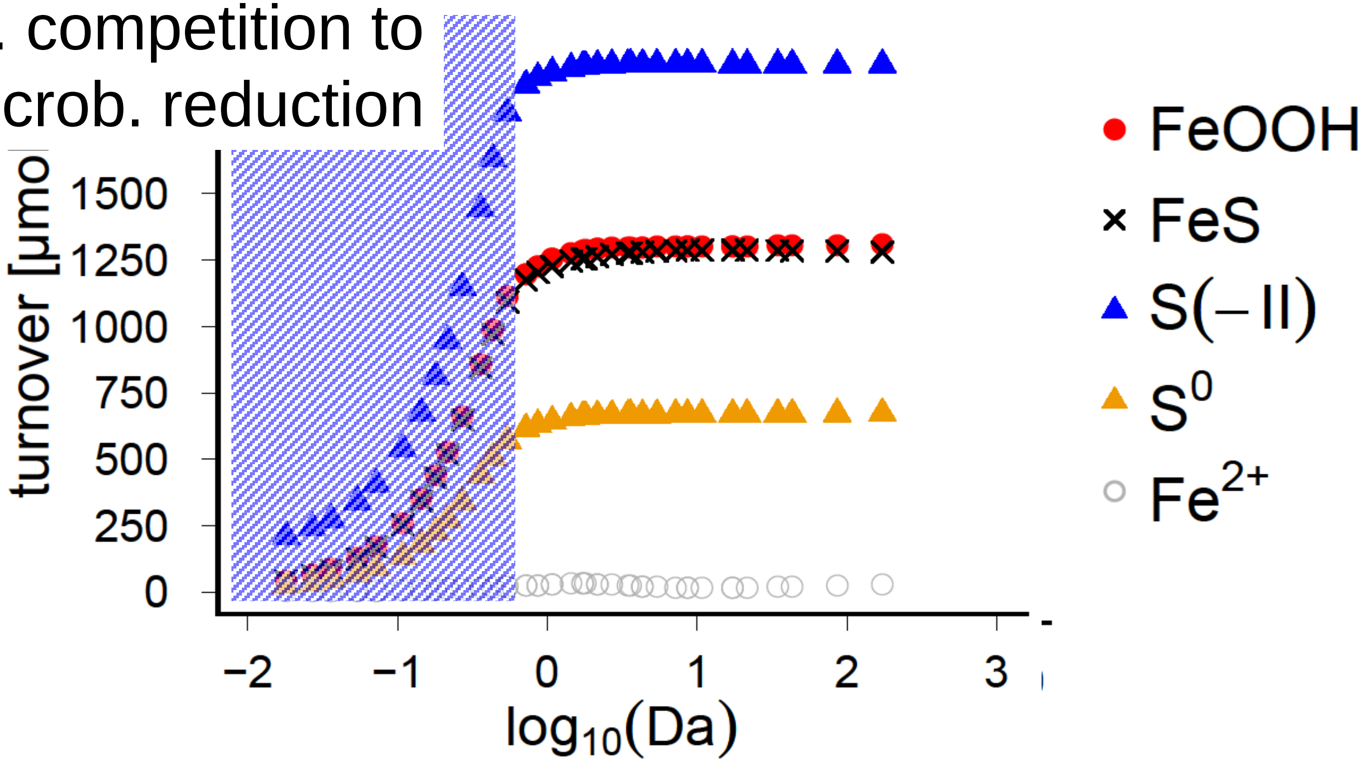
- simulations with TBC -



transport ↔ reaction

Turnover related to Damköhler Numbers
- simulations with TBC -

e. g. competition to microb. reduction



transport ↔ reaction

Physical and chemical restrictions ….

- pH
- Temperature
- c(surface sites)

$$\text{Da} = \frac{\text{Reaction rate (mass/time)}}{\text{Transport rate (mass/time)}}$$

- hydr. conductivity
- gradients

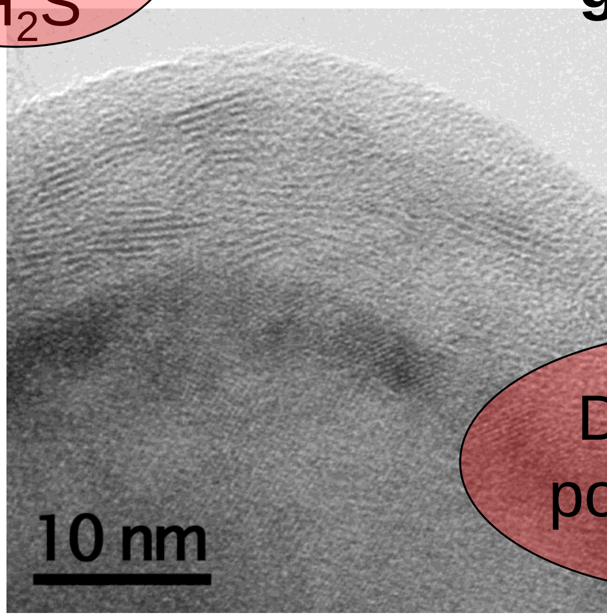
Local variations

… create patchiness !

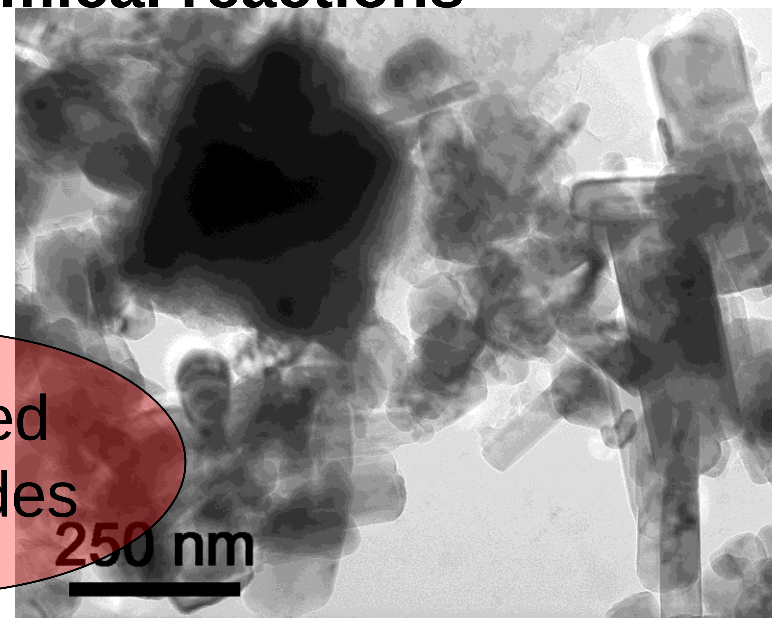
Summary

Dissolved H_2S

1) Microscale process-steps decide on the relative importance of transport for (bio-) geochemical reactions



Dissolved polysulfides

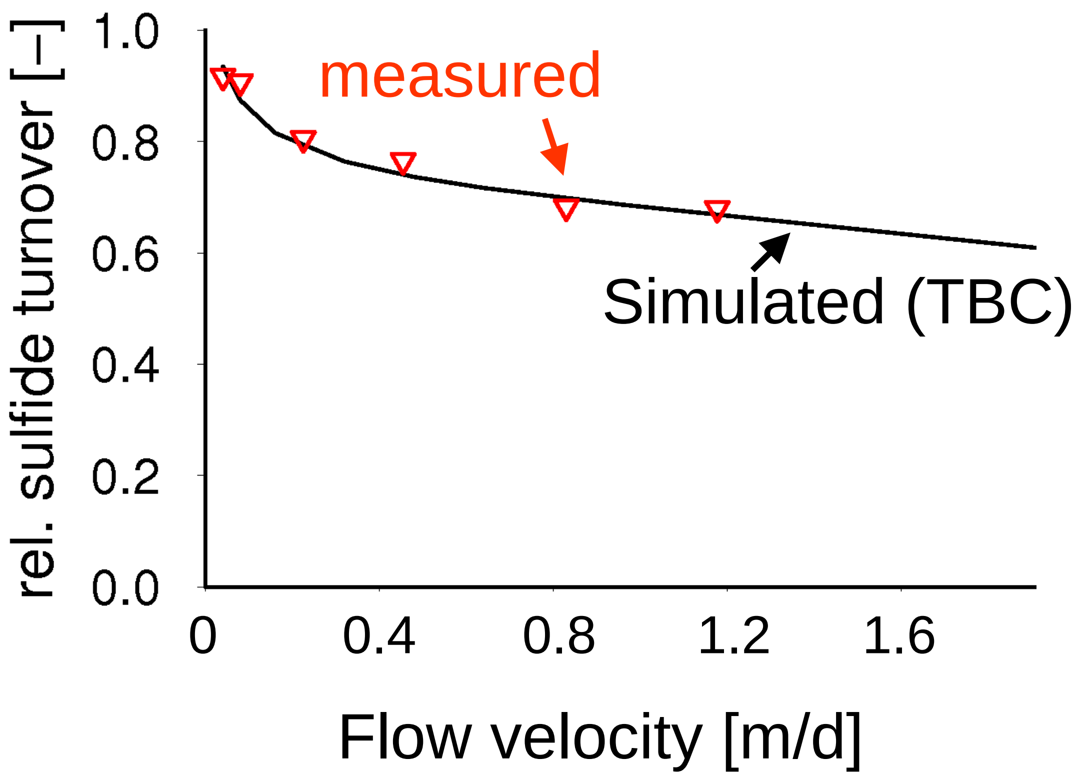


Surface bound FeS

Precipitation of a new phase

Summary

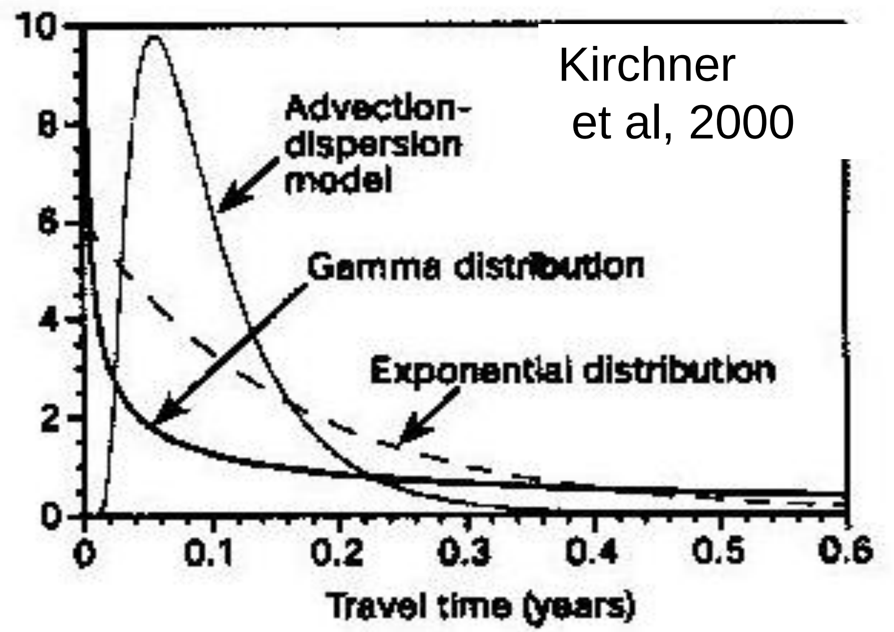
2) Residence times control turnover rates



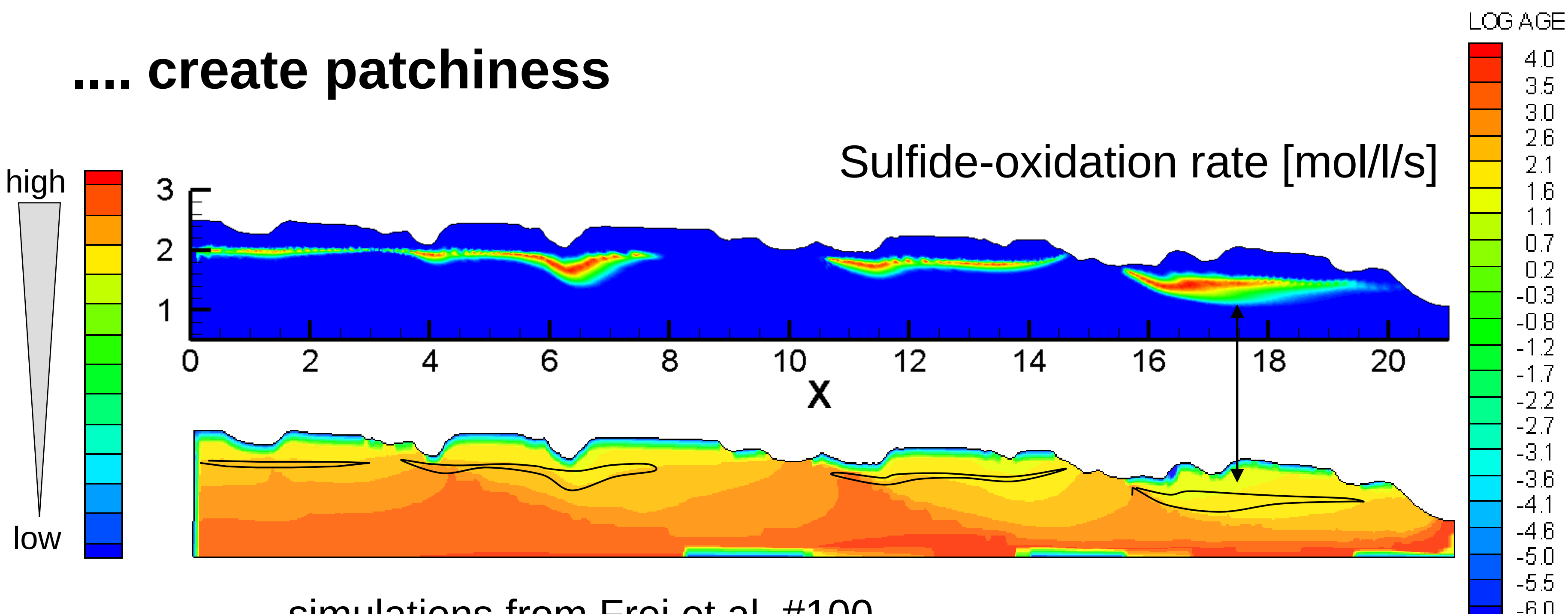
Summary

3) Distribution of residence time

and kinetic parameters



.... create patchiness



simulations from Frei et al, #100

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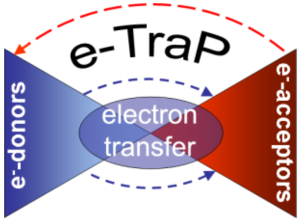
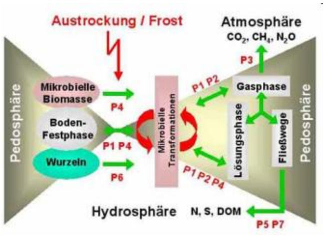
Acknowledgements

DFG Research Unit 580
electron transfer processes in anoxic aquifers



DFG Research Group 562
soil processes under extreme meteorological boundary conditions



Geotechnology Research Programme
(German Ministry of Education and Research)

GEOTECHNOLOGIEN

Position announcement

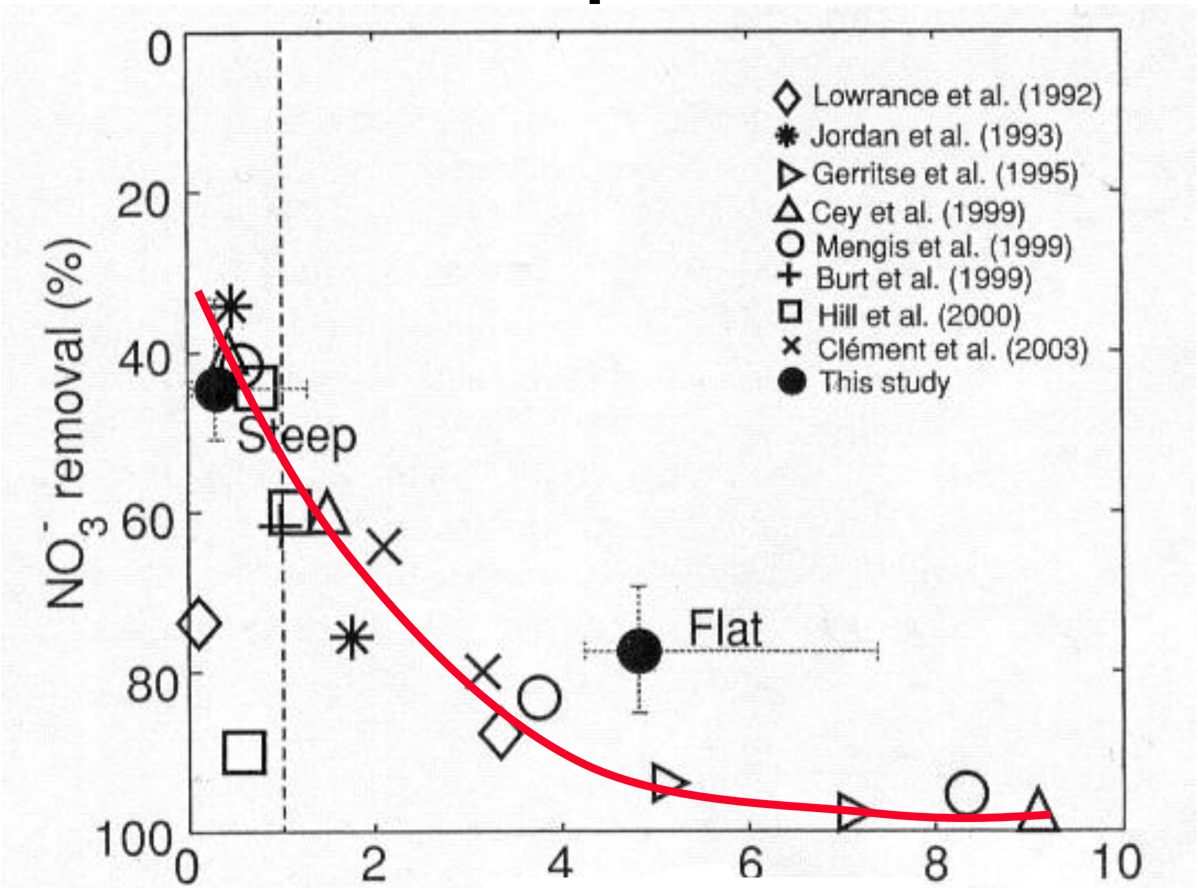
Assistant professor in ecohydrology

Department of Hydrology

BayCEER

University of Bayreuth

Application of Damköhler numbers
Nitrate removal in the riparian zone



$$Da = \tau / t_r$$

Ocampo et al, Water Res. Res, 42, 2006

Complilation of data

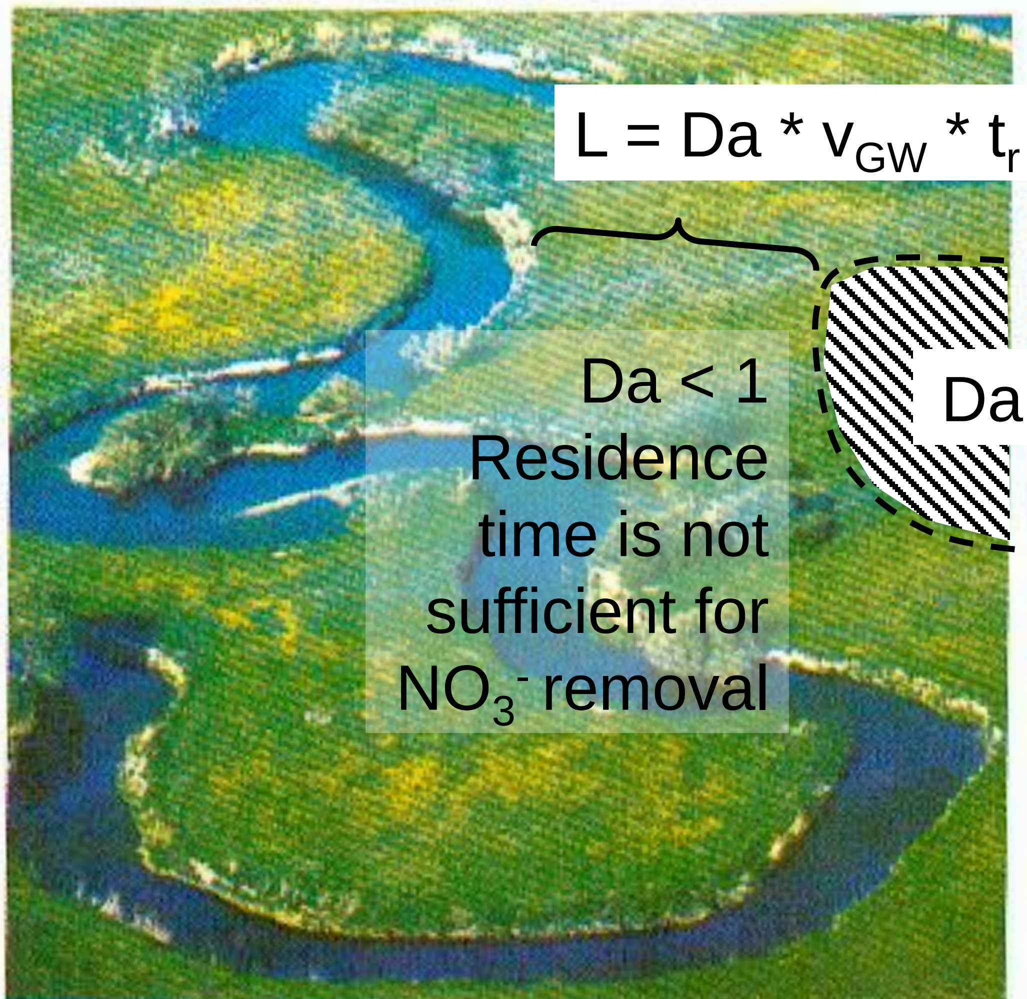
Ocampo et al, Water Res. Res, 42, 2006

- t_r characteristic reaction time derived from field data and adv. disp. reaction modelling
- L distance of nitrate concentration gradient
- V_{GW} GW flow-velocity from field data

$$Da = (L/v_{GW}) / t_r$$

Application of Damköhler numbers

Mapping of nitrate-removing riparian zones



Consumption of S° + HCl-extractable Fe(II) after two days