

Modeling on uranium geochemistry and spent fuel

Sonia Salah / Christelle Cachoir

Waste & Disposal Department

SCK•CEN

Validation

Model

Numerical model

Conceptual model

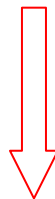
General understanding of the system

Confidence

Model validation

Natural phenomena

long-term processes



Numerical model

applicability

limitations



Laboratory experiments

short-term processes

Oklo – Phenomenon

Natural “fossil” nuclear fission reactor

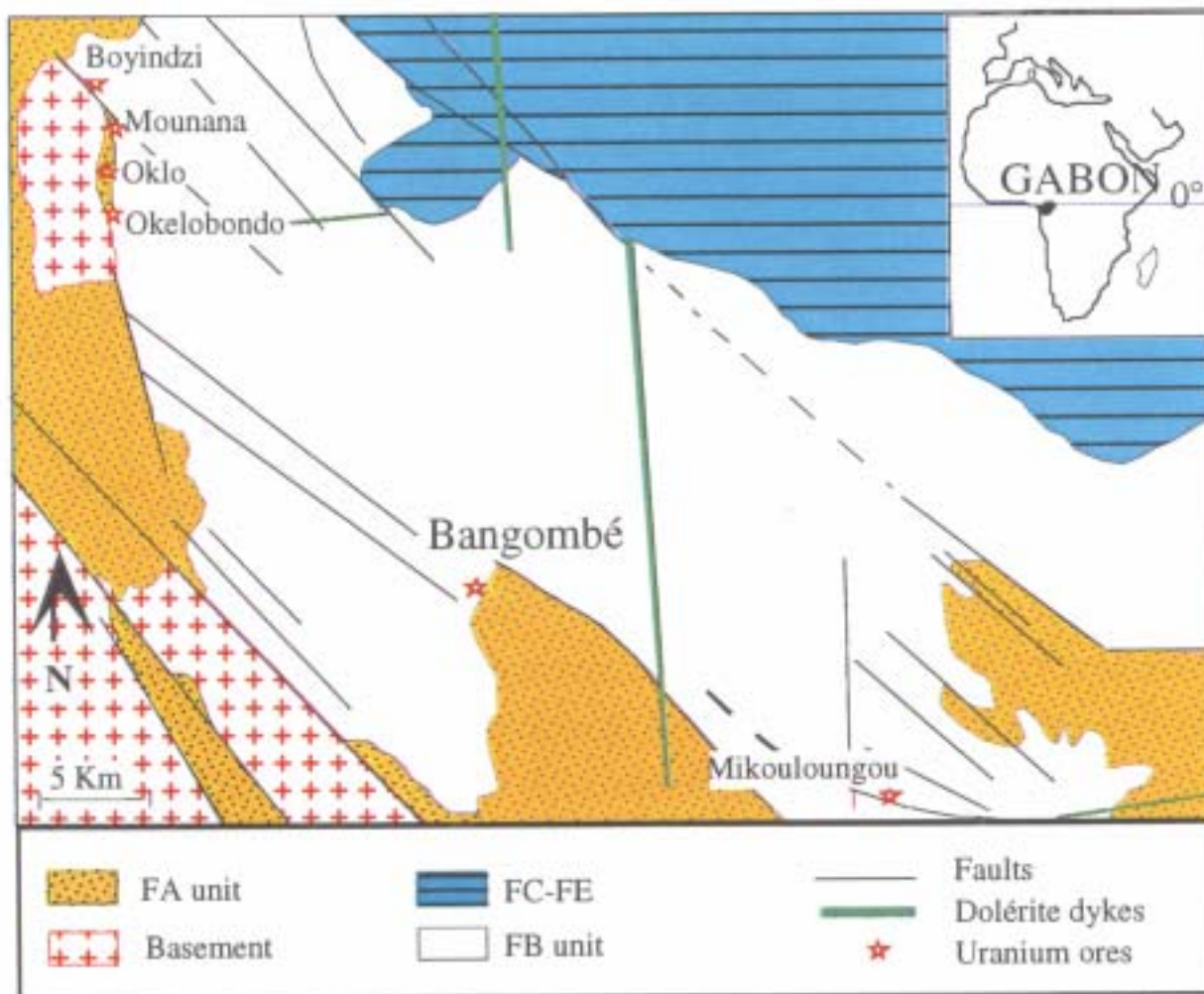


Uranium mineralization

1950 My



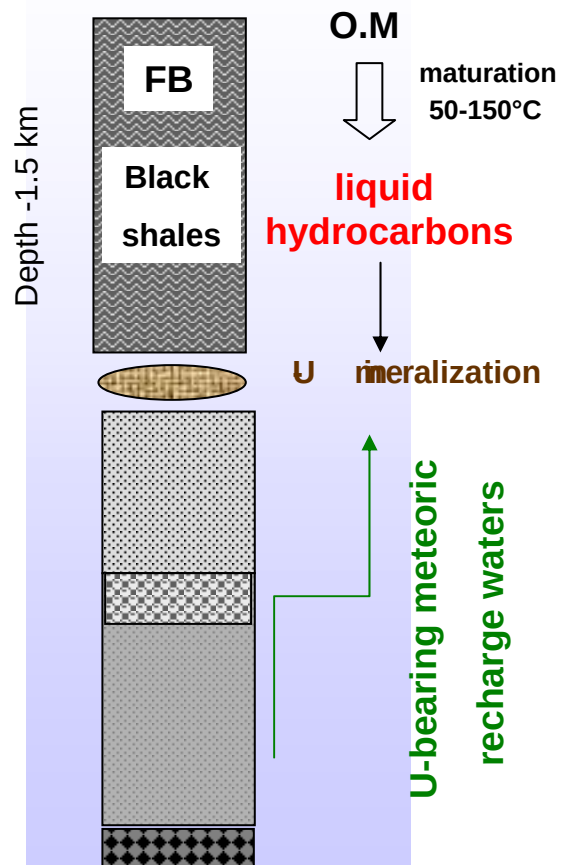
Location of uranium ore deposits



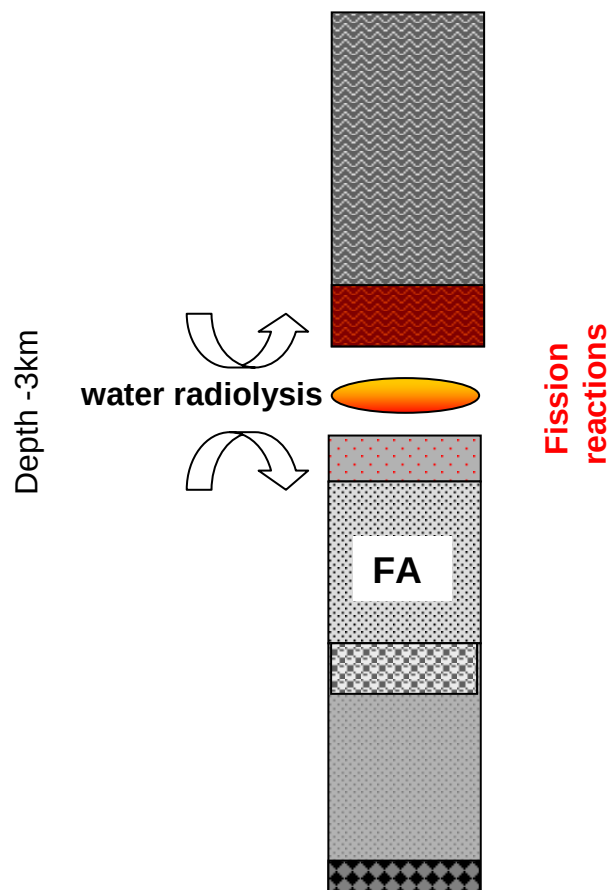
History

2050 My Ore-stage

burial and hydraulic fracturing

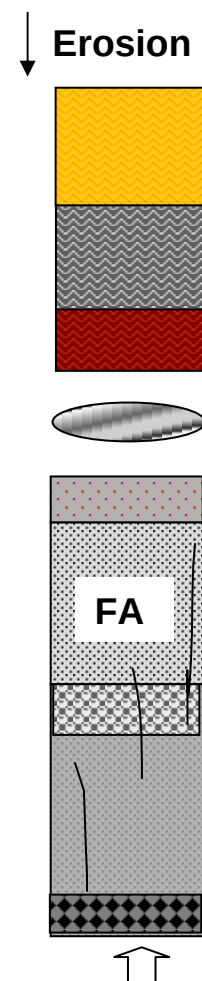


1970 My Reactive stage



350 Ky Post-ore stage

Onset of supergene weathering



Problem of radioactive waste disposal

Oklo/Bangombé

high-grade uranium ore deposit

Natural analogue



**Nuclear waste
storage site**

Definition (Côme and Chapman, 1986)

“An occurrence of materials and processes which resemble those expected in a proposed repository”

Uraninites of reactor core

spent fuel produced in artificial power plants



**UO₂-dissolution rates under
repository relevant conditions**

Hydrothermal clay halo

Bentonite ➤ backfill, buffer material
host rock of the repository



**Retention properties of clays, alteration
and transformation processes**

Organic matter/graphitic bitumen

“Technical” bitumen proposed as immobilizing matrix



**Degradation (microbiological and/or radiation induced) processes
and retention capacity**

PROCESSSES

Elapsed time



Long-term behaviour of radionuclides

= Release, transport and retardation processes

Effects of water radiolysis (=decomposition of water)

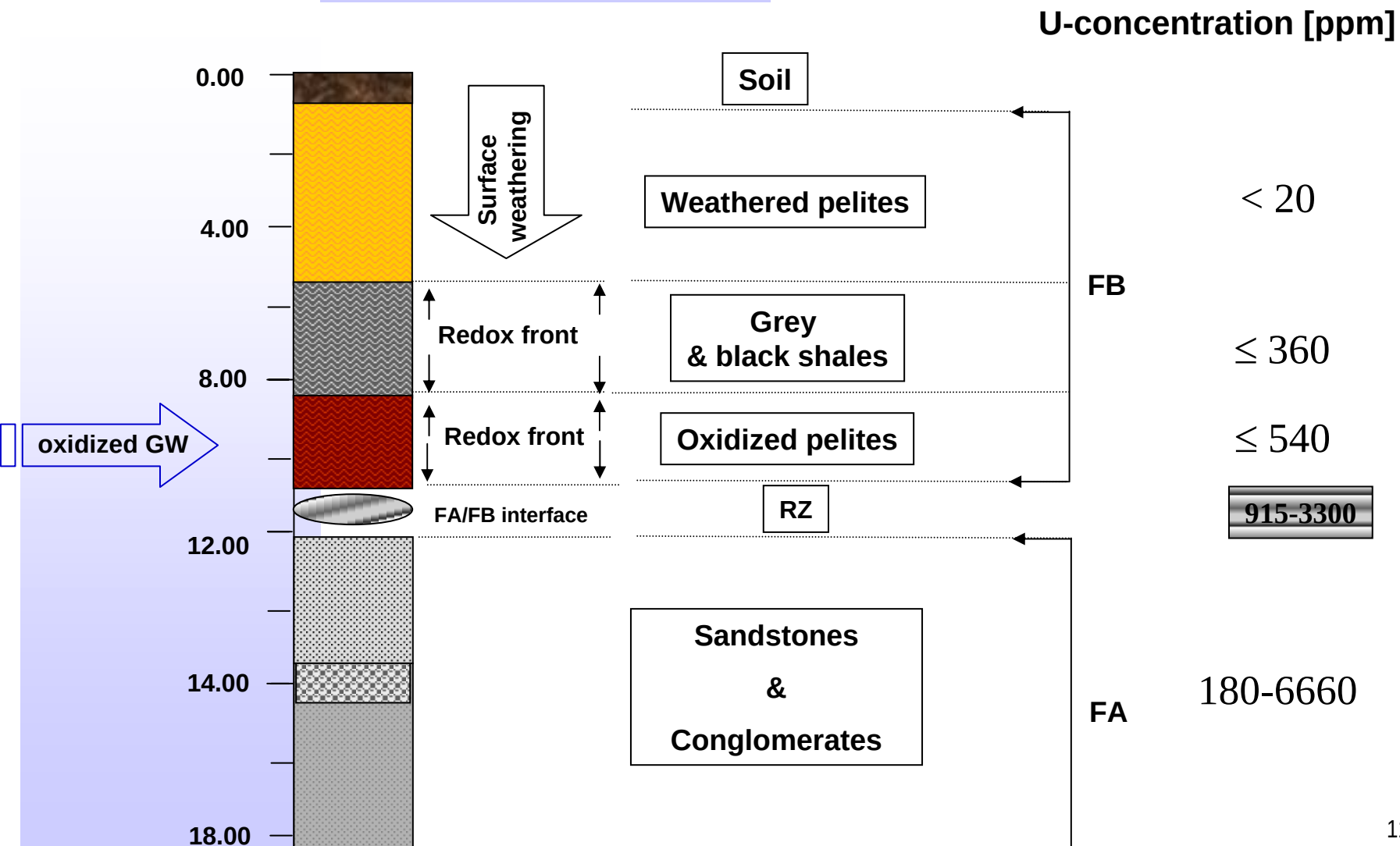


e.g. oxidation phenomena

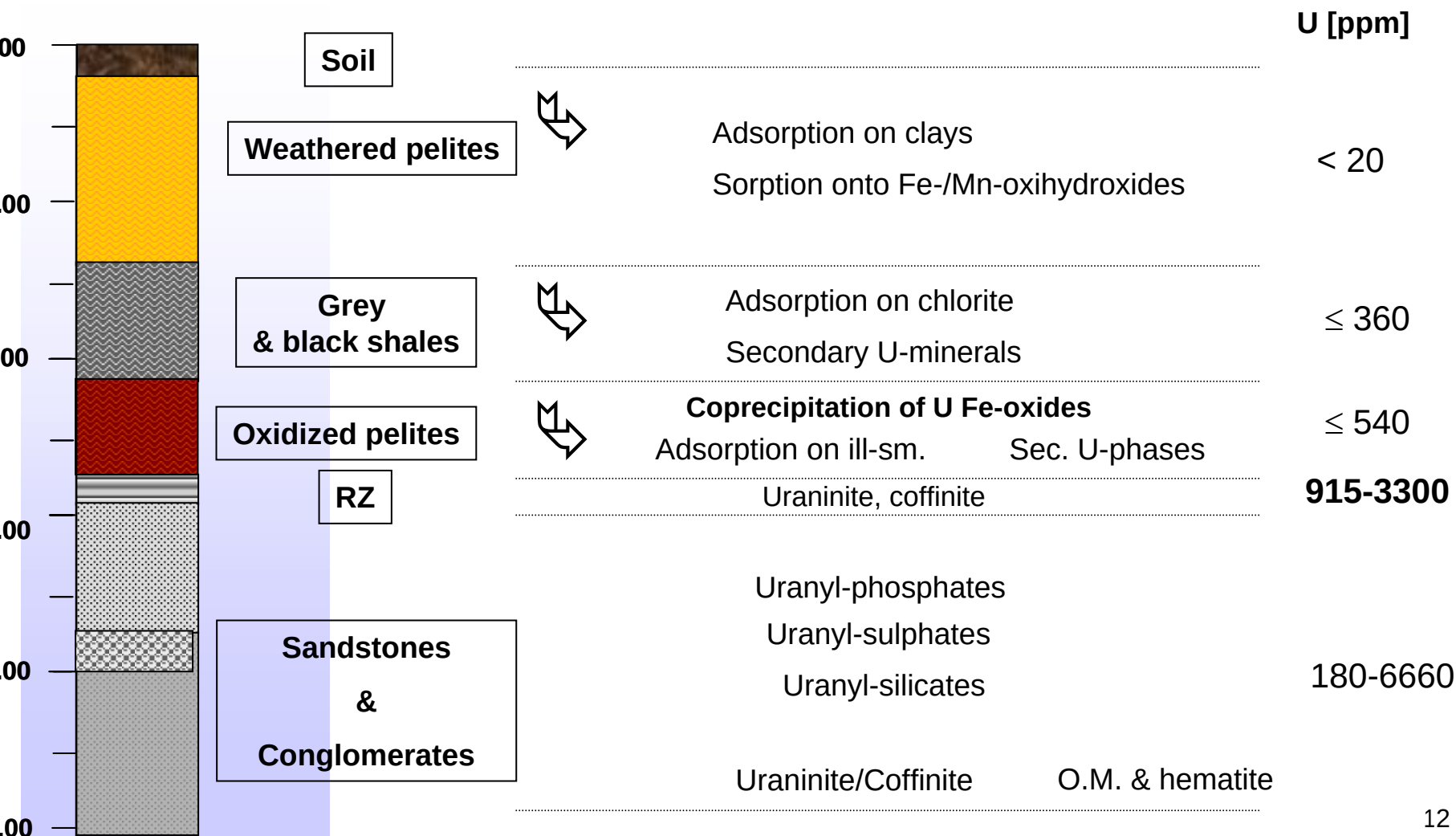
Modeling example

Present day U-migration/retention processes

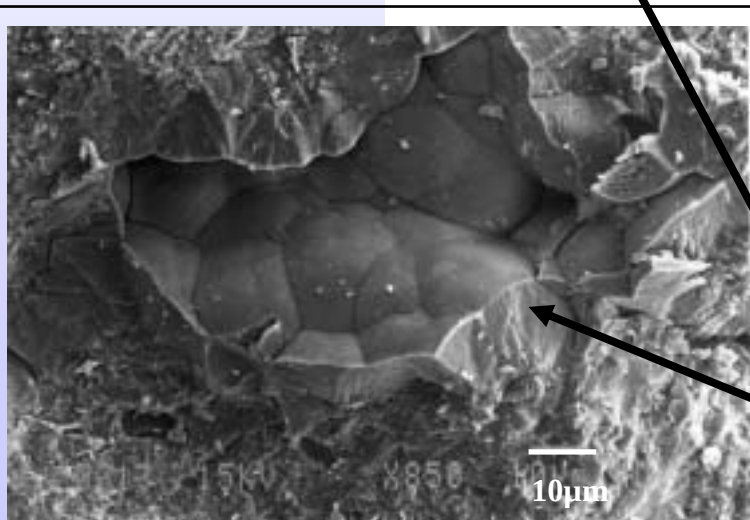
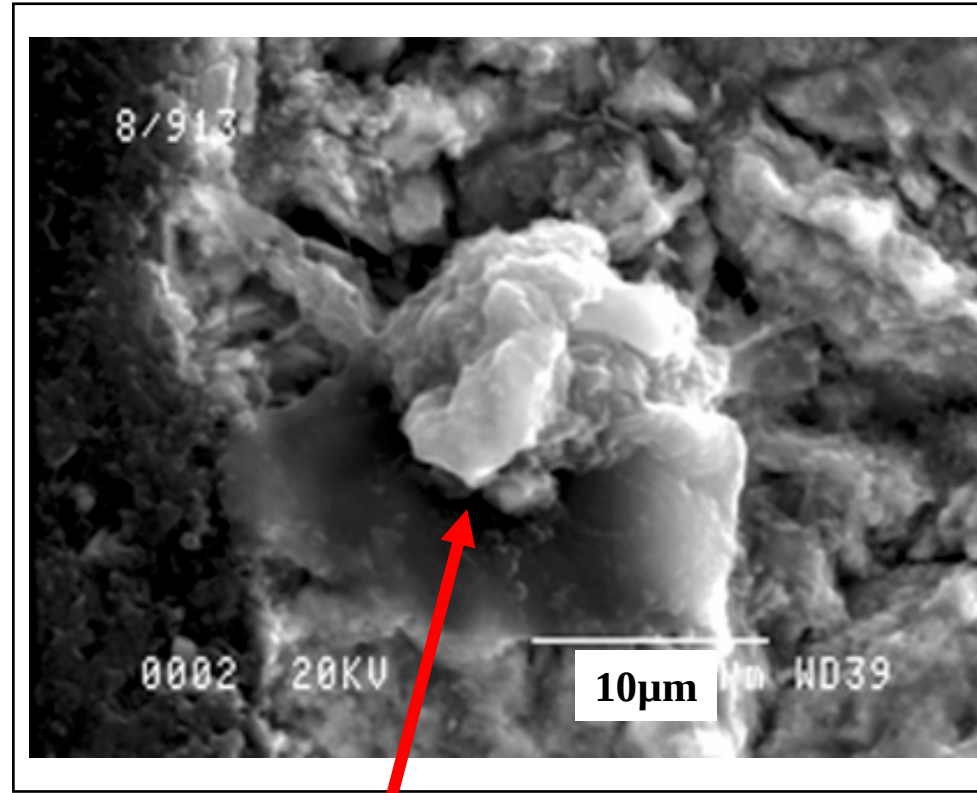
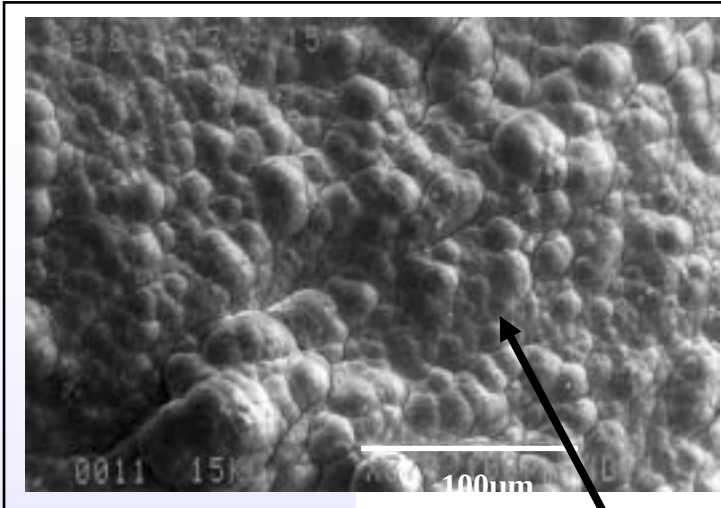
U-distribution in the rocks



U-retention mechanisms



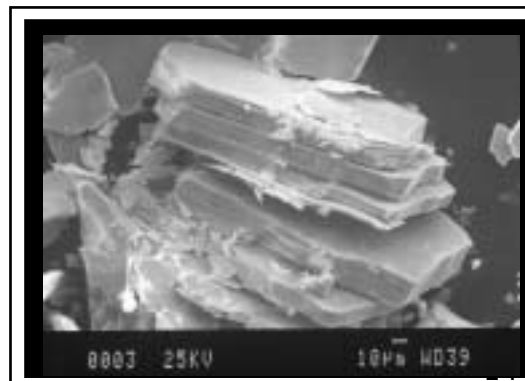
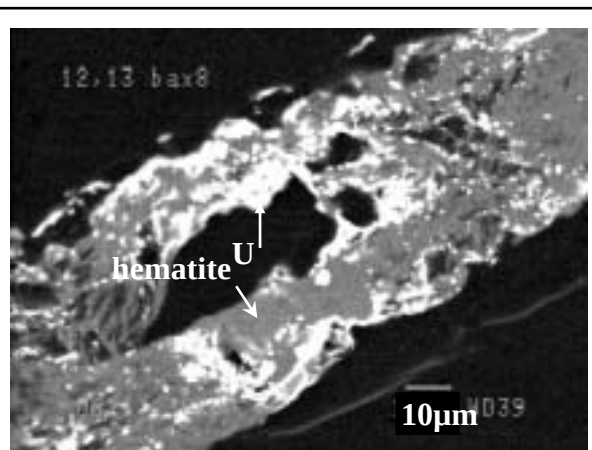
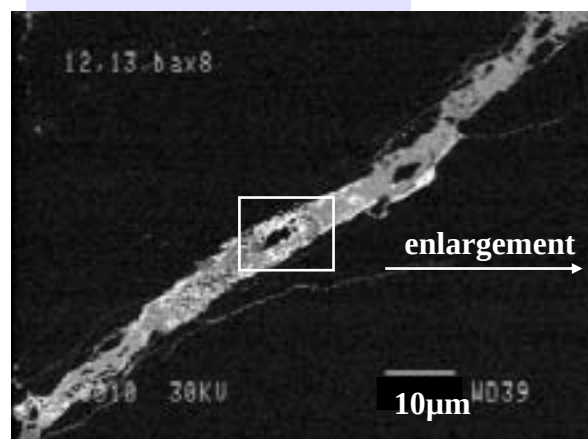
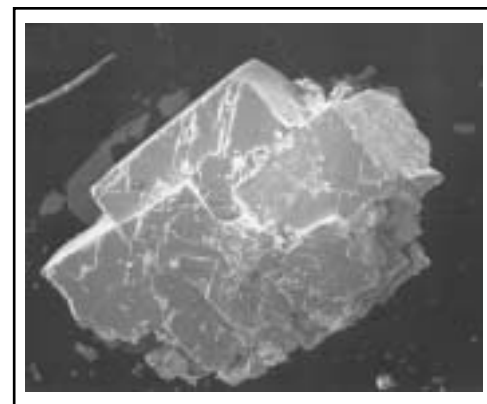
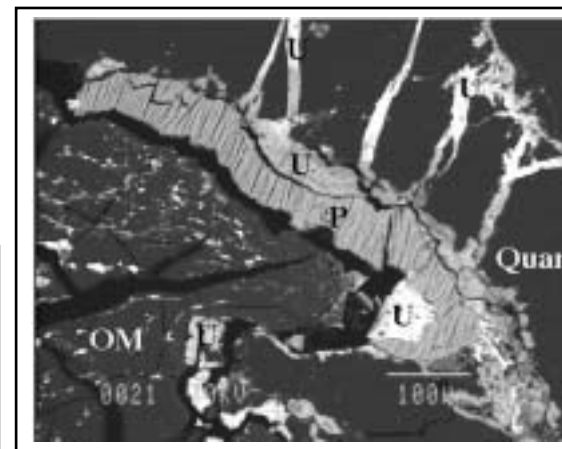
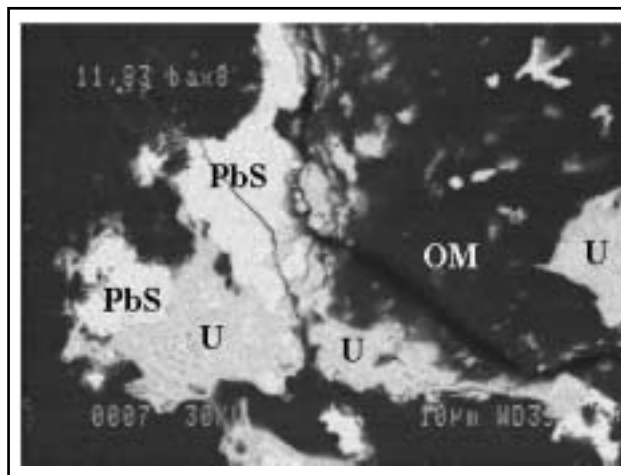
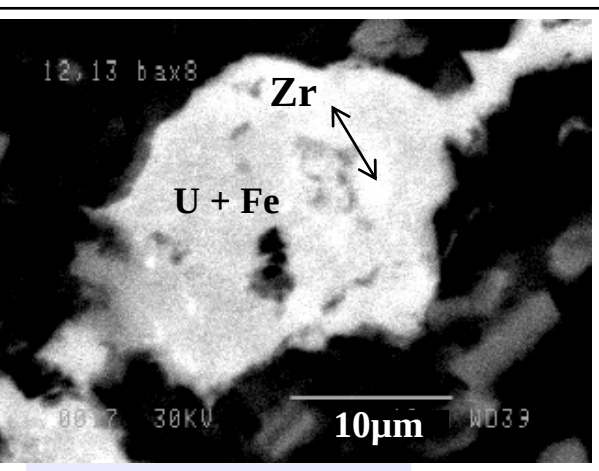
SEM images of oxidized pelites FA/FB interface



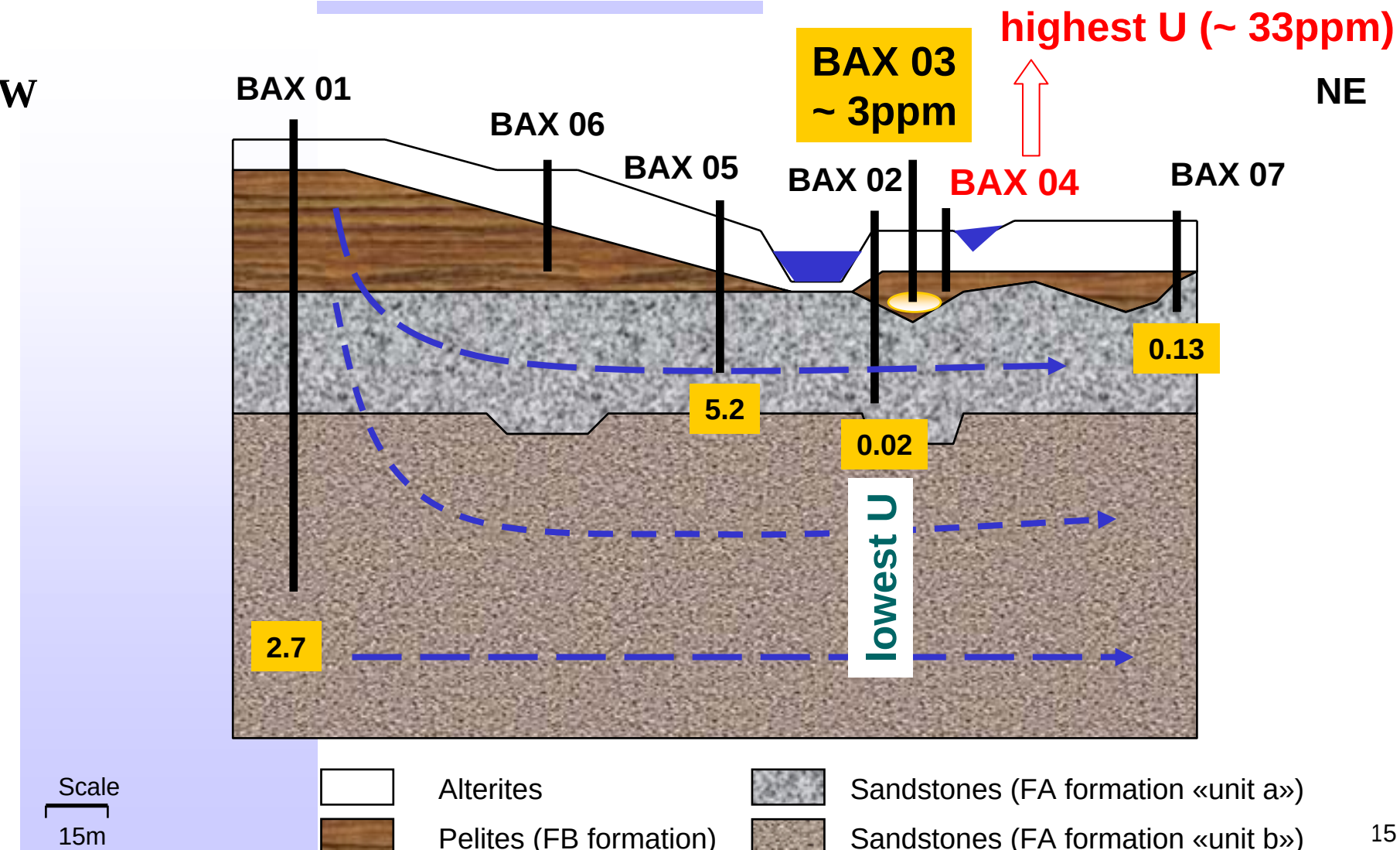
“autunite - like” overgrowth

Spherical goethite aggregates

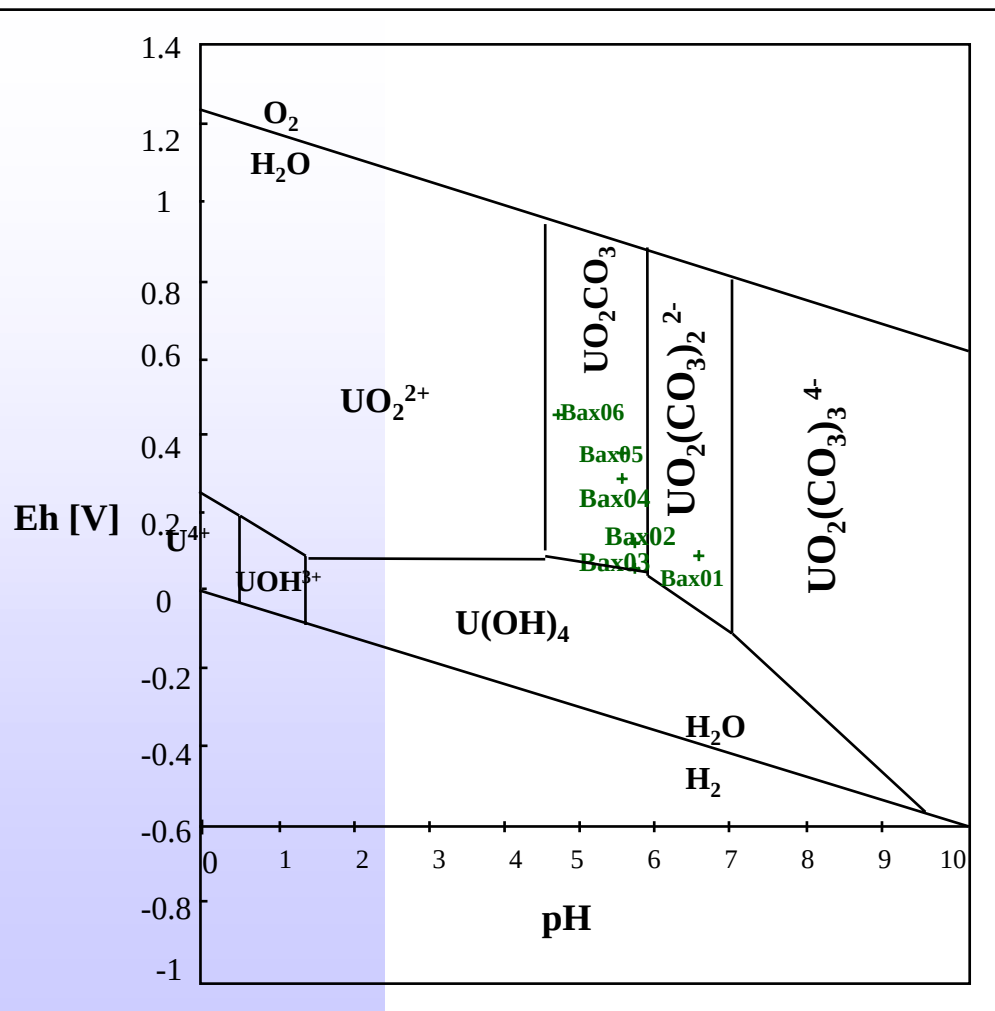
FA formation



U-concentrations [$\mu\text{g/L}$] in the Bangombé groundwaters



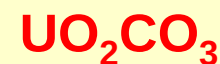
Calculation of aqueous U-speciation



Dominant aq. U-species



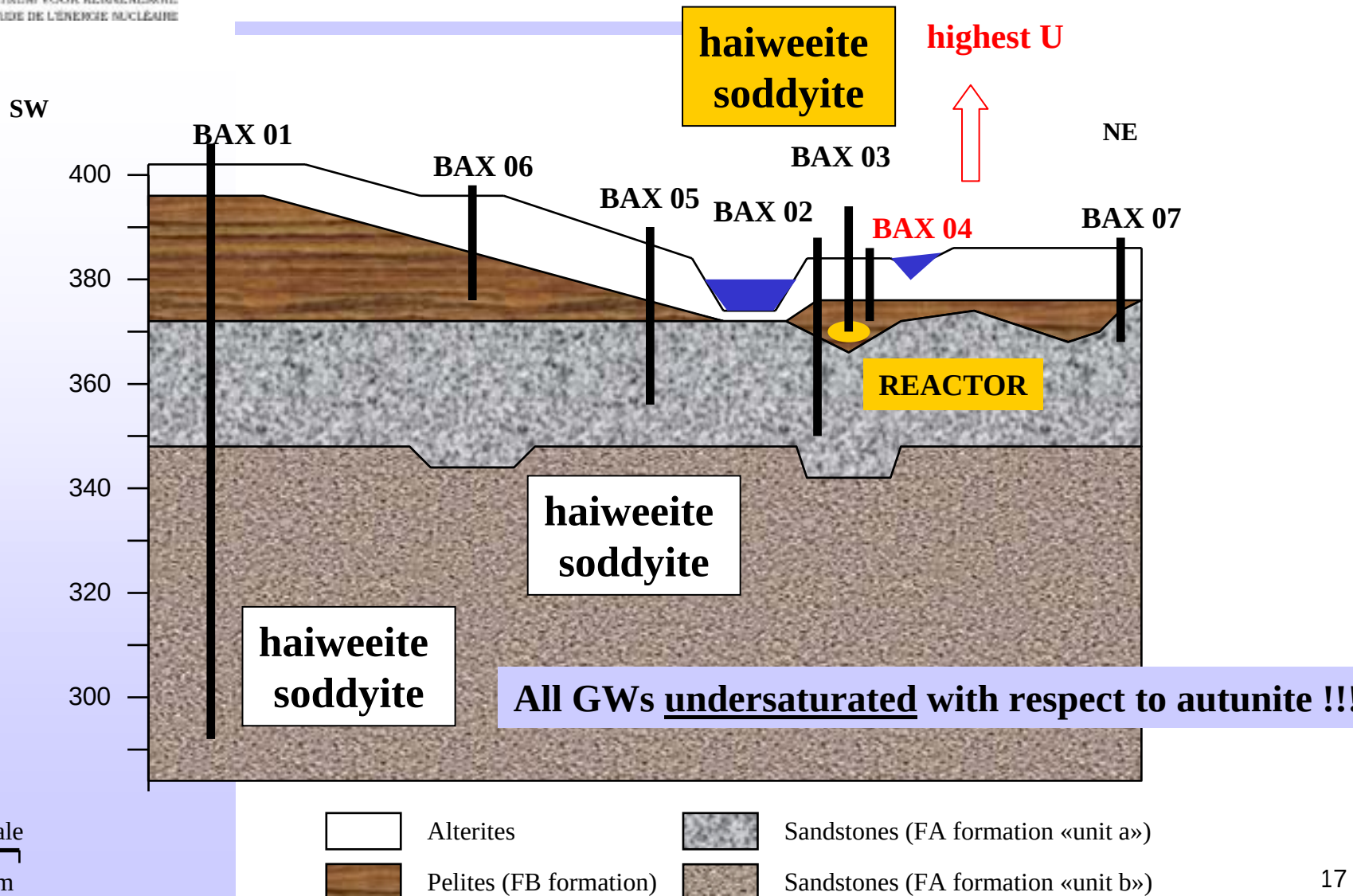
Uranyl-carbonate-complexes



and



Calculation of saturation indices for U-minerals



Results of SI calculations for other minerals BAX 04

Silica

water saturated with respect to quartz

Aluminum

**water slightly undersaturated with respect to
amorphous $\text{Al}(\text{OH})_3$**

Iron

**close to equilibrium with amorphous $\text{Fe}(\text{OH})_3$
and undersaturated concerning siderite**

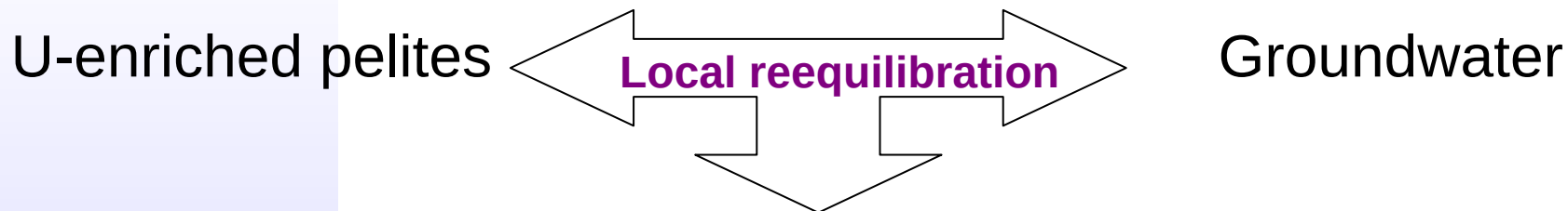


**Redox control exerted by FeII/FeIII redox pair
dissolution of siderite and precipitation of amorphous iron oxide
governing $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio**

Question

**How can the higher U-concentrations
downstream the RZ be explained ?**

Assumption



Elevated U migrating in the groundwater ?

Modeling of present day U-migration/retention

Code: KINDIS (Fritz, 1981), thermodynamic approach

PELITE COMPOSITION:

Clays:	illite, clinochlore, daphnite, kaolinite
Carbonates:	siderites, dolomite, rhodochrosite
Other:	quartz, goethite, albite
U-phases:	uraninite, autunite

GROUNDWATER COMPOSITION:

BAX07 (= initially poorly concentrated water comp.)

SECONDARY PHASES:

Amorphous $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, SiO_2
Uranyl-silicates/-phosphates and uranium oxides

←
←
maintained in contact



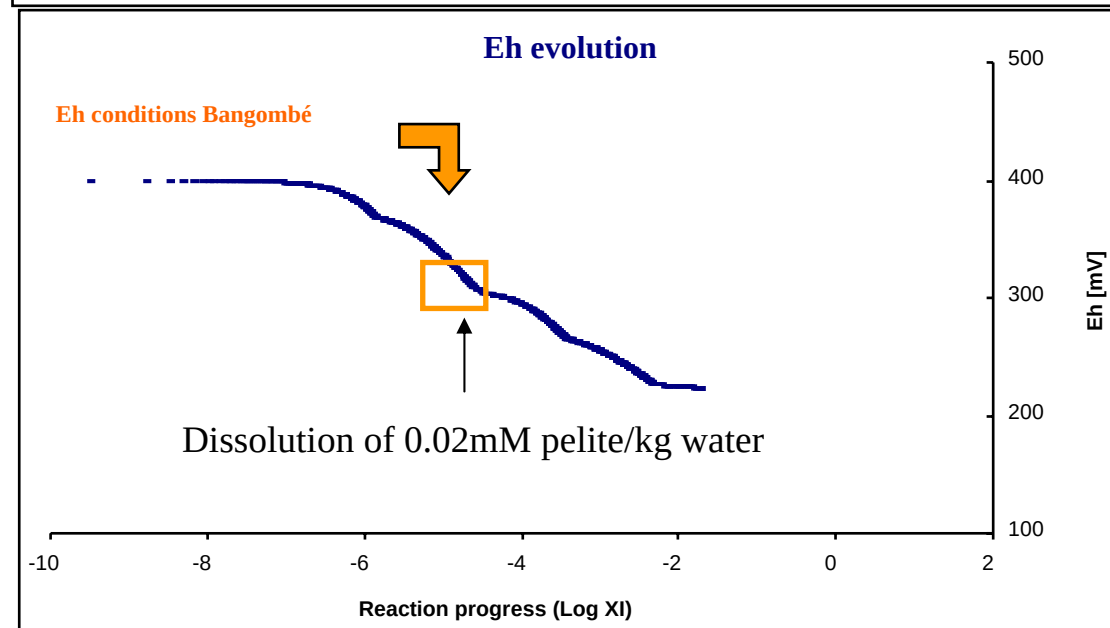
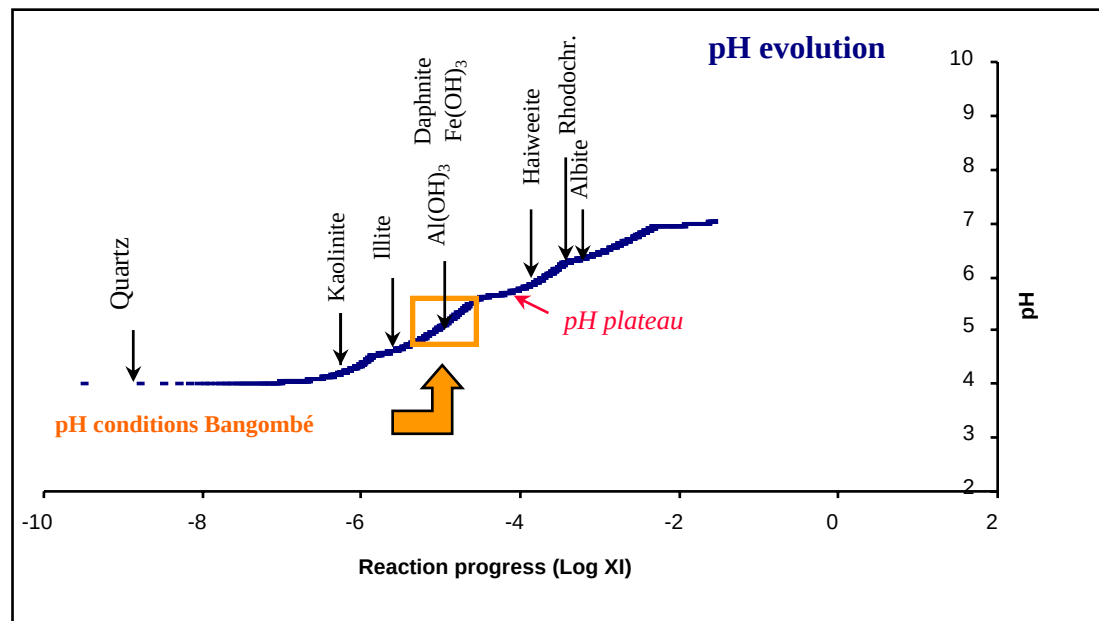
Primary minerals suppressed to precipitate

Results of dissolution test

$$-4,69 < \text{LogXI} < -3,99$$

Eh-pH domain of BAX04

(Eh=297, pH=5,76)



RESULTS

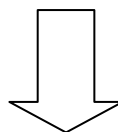
-4,69 < XI < -3,99 Eh-pH domain of BAX04 (Eh=297,pH=5,76)

Si, Fe, Mn:	Measured and simulated conc. in the same order of magnitude	
HCO ₃ ⁻ :	Simulated conc. slightly lower than measured values	
K, Na, Al:	Higher than measured values	
U:	41 and 208 µg/L	measured: 33 µg/L

Results reflect ability to reproduce quite well the high U-concentrations in the field by assuming only local dissolution of trace amounts of uranium minerals occurring in the red pelites.

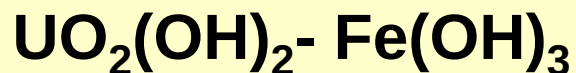
Model improvement

U-retention in red pelites



Coprecipitation of U with iron oxides/oxyhydroxides

Ideal binary U-Fe solid solution (Bruno et al., 1995):



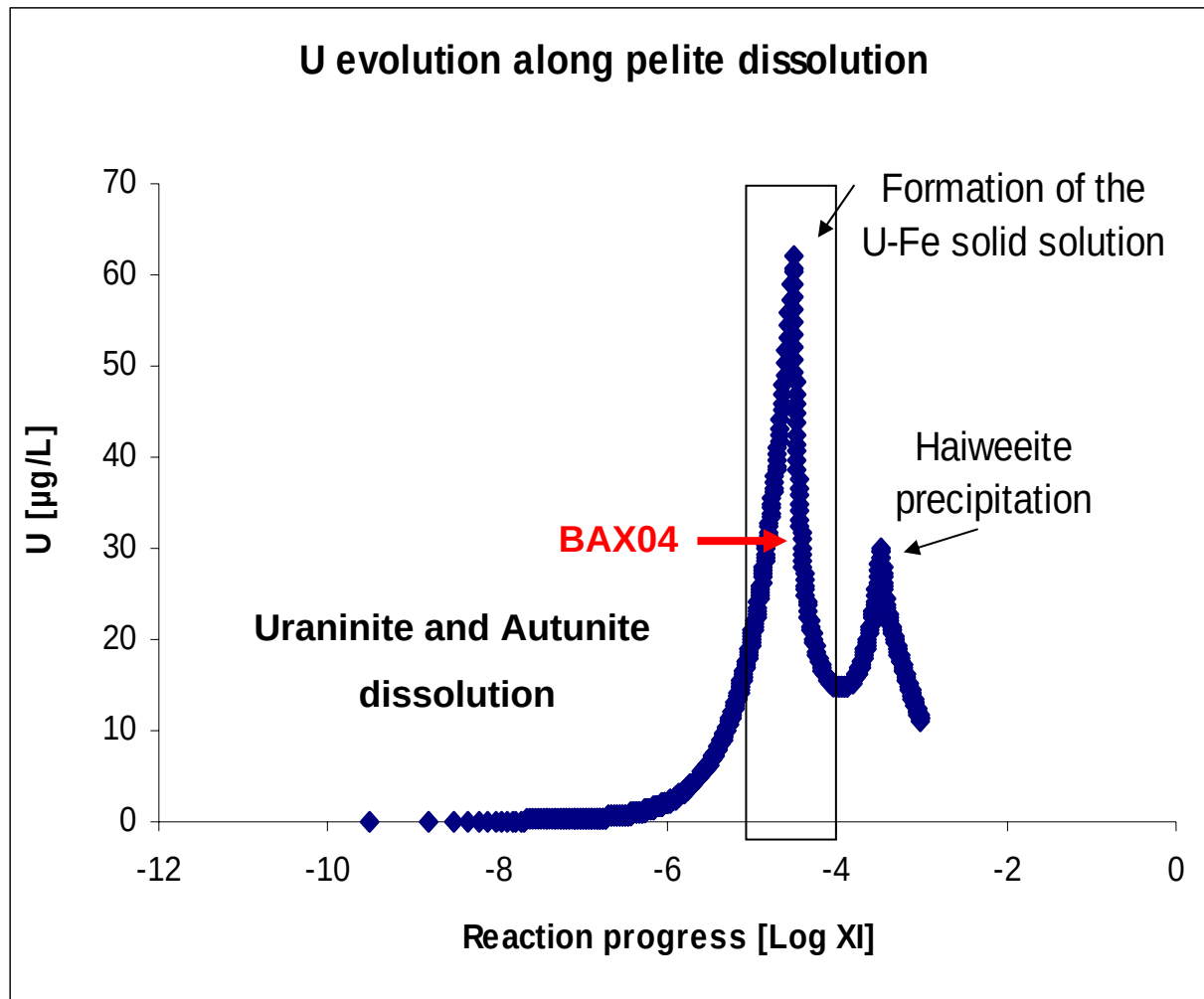
Results

$-4,69 < XI < -3,99$

Eh-pH domain BAX04

U = 9 and 44 µg/L
simulated

33 µg/L
measured



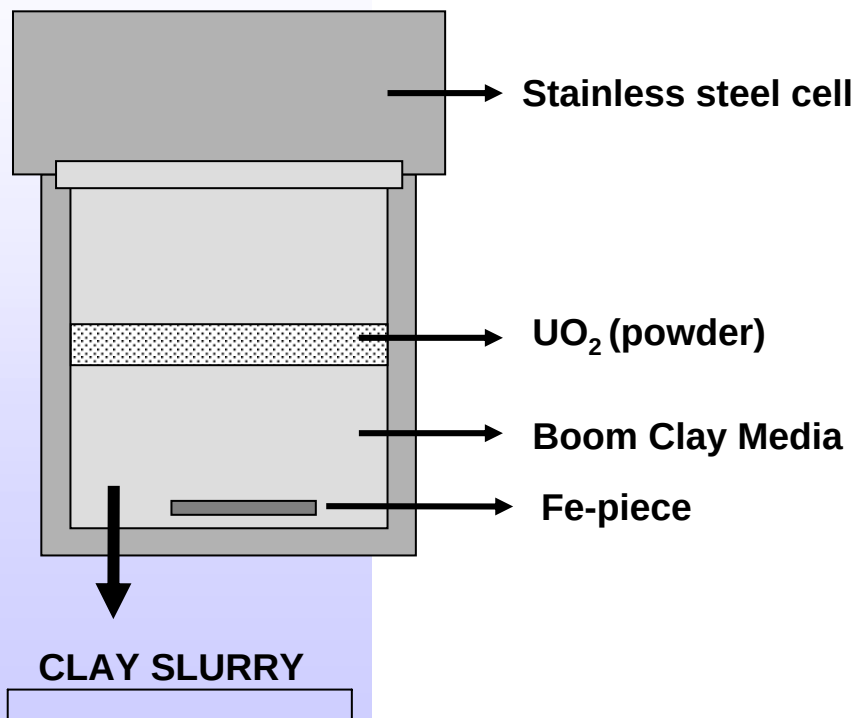
Conclusions

The high U-concentrations in the field can be quite well reproduced by assuming only local dissolution of trace amounts of uranium minerals occurring in the red pelites.

However, introducing the formation of a U-Fe solid solution in the model leads to a better consistency between the simulated and measured U-concentration

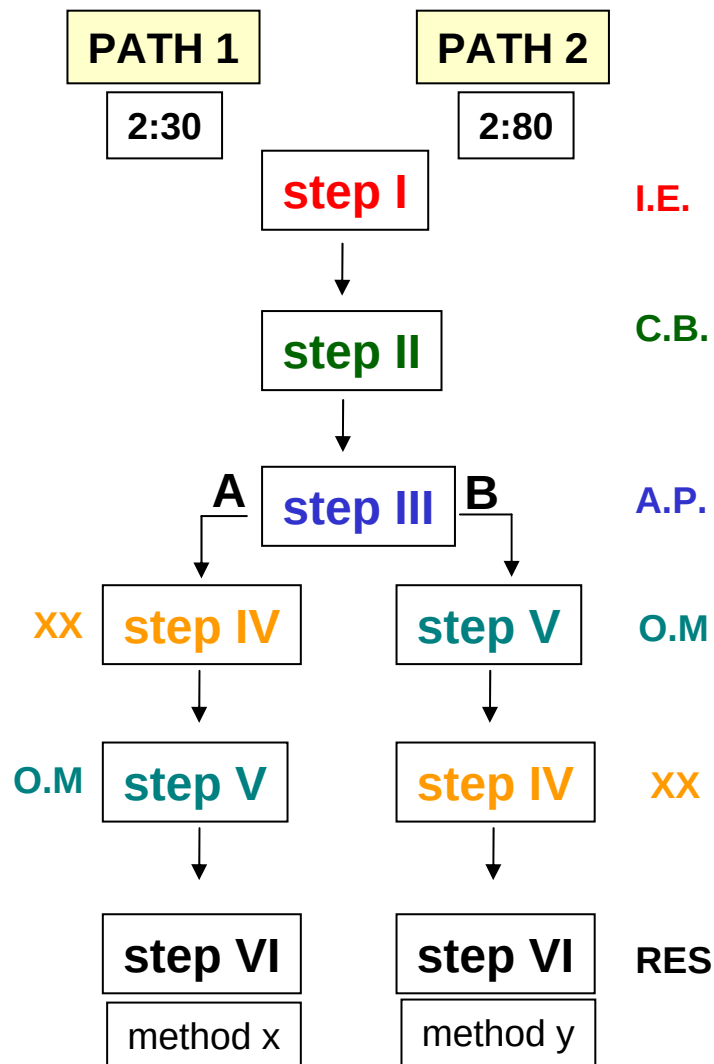
Static dissolution experiments & Sequential extraction experiments

Static dissolution tests of α -doped UO_2 in Boom Clay conditions



Clay analysis

Leachate analysis



Objectives of experimental studies



Determine dissolution rates of α -doped UO_2 in different Boom clay media



Investigate influence of α -activity on the UO_2 dissolution rates

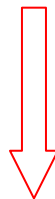


Get mechanistic understanding of U-retention/migration processes

Model validation

Natural phenomena

long-term processes



Numerical model

applicability

limitations



Laboratory experiments

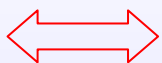
short-term processes

 **Results of this approach will be presented
in the next Exchange meeting....** 

Thanks for your attention...

U-concentrations [$\mu\text{g/L}$] in the Bangombé groundwaters

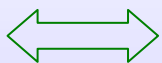
Reactor
water



BAX03 pe

3.1

Downstream
the RZ



BAX04 ss

33.6

BAX05 ss

5.2

BAX06 pe

n.d.

BAX07 ss

0.13

Results



Aqueous U in shallow and deeper groundwaters controlled by uranyl-silicates

consistant with microscopic observations



No solubility limiting mineral was determined for intermediate surface water (= lowest U conc.) and water sampled downstream the reactor zone (BAX04, highest U-conc.)

U-retention in the pelitic horizon mainly due to coprecipitation processes with iron oxides and oxyhydroxides



All groundwaters undersaturated with respect to autunite, indicating that autunite nowadays is rather a dissolving than a forming mineral phase

Coupling geochemistry and mass transfer with fluid flow

Diederik Jacques

- Coupled reactive transport models (RTM)
 - What/why/applications
- RTM – contaminant hydrological models
 - Example: Cd leaching in a soil profile
- RTM – reaction path/geochemical models
 - Example: alkaline fluid through Boom Clay
- Applications in deep disposal
- Conclusion

Coupled reactive transport models What?

- Tools to model simultaneously:
 - (Water flow)
 - Transport of solutes and contaminants
 - Biogeochemical reactions
- in porous media (geological layers / soils)

Coupled reactive transport models

Why?

- Geochemical reactions typically occur in open systems where fluxes drive reactions
- Difficult to evaluate quantitatively the importance of time-dependent processes without considering them as part of a coupled system
- Models can provide quantitative tests of hypotheses

Coupled reactive transport models Applications

- Chemical weathering
- Contaminant hydrogeology /
hydrogeochemistry
- Remediation design
- Assessing effects of “perturbations” on
geochemical conditions
- Transport of radionuclides

Fully coupled models versus 'classical' contaminant hydrological models

- Ability to consider mechanistic models for adsorption / surface complexation and their effect on contaminant mobility
- Aqueous complexation and speciation effects on contaminant mobility
- Conversion of contaminants via (bio)chemical reactions
- Dissolution/precipitation and effect on adsorption

Example: Cd leaching in a soil profile

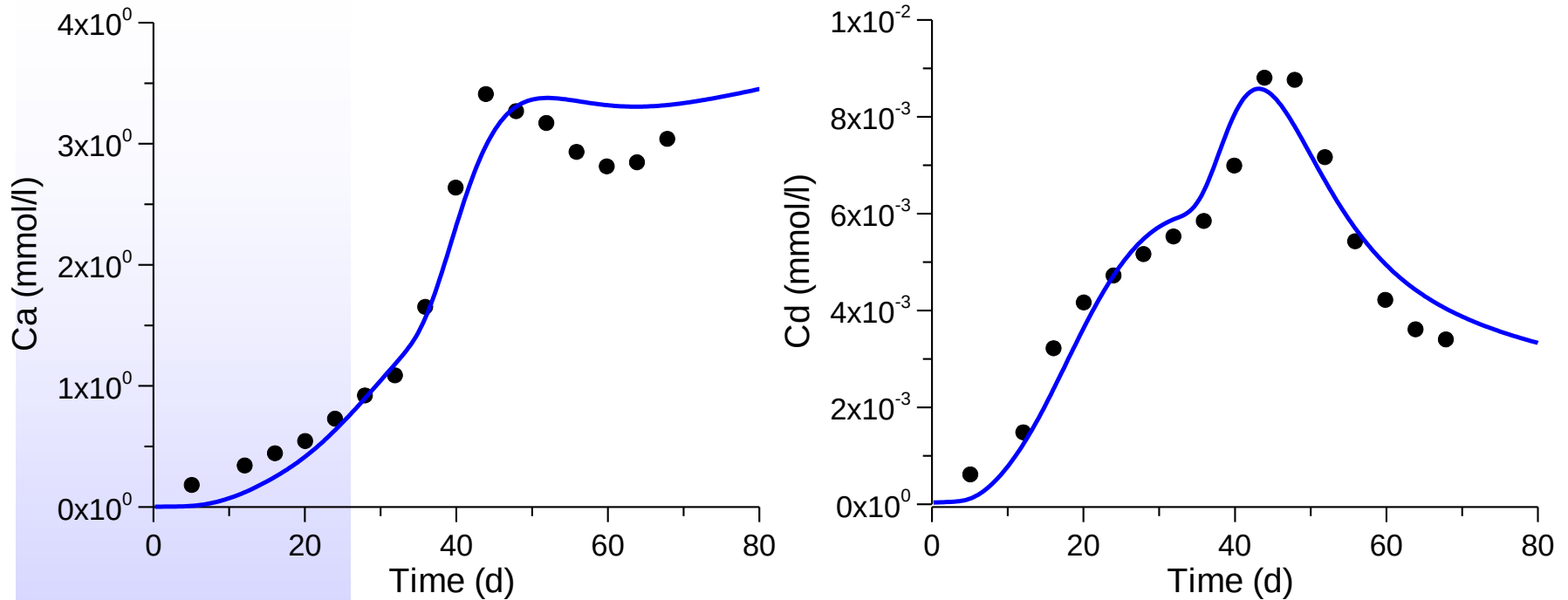
Problem definition



- Podzol (Kempen) contaminated with heavy metals (Cd, Zn, Pb)
- Lysimeter (80 cm diameter, 100 cm long)
- Equipped with TDR probes
- Bottom: grid based wick sampler system
- Experiment: boundary conditions

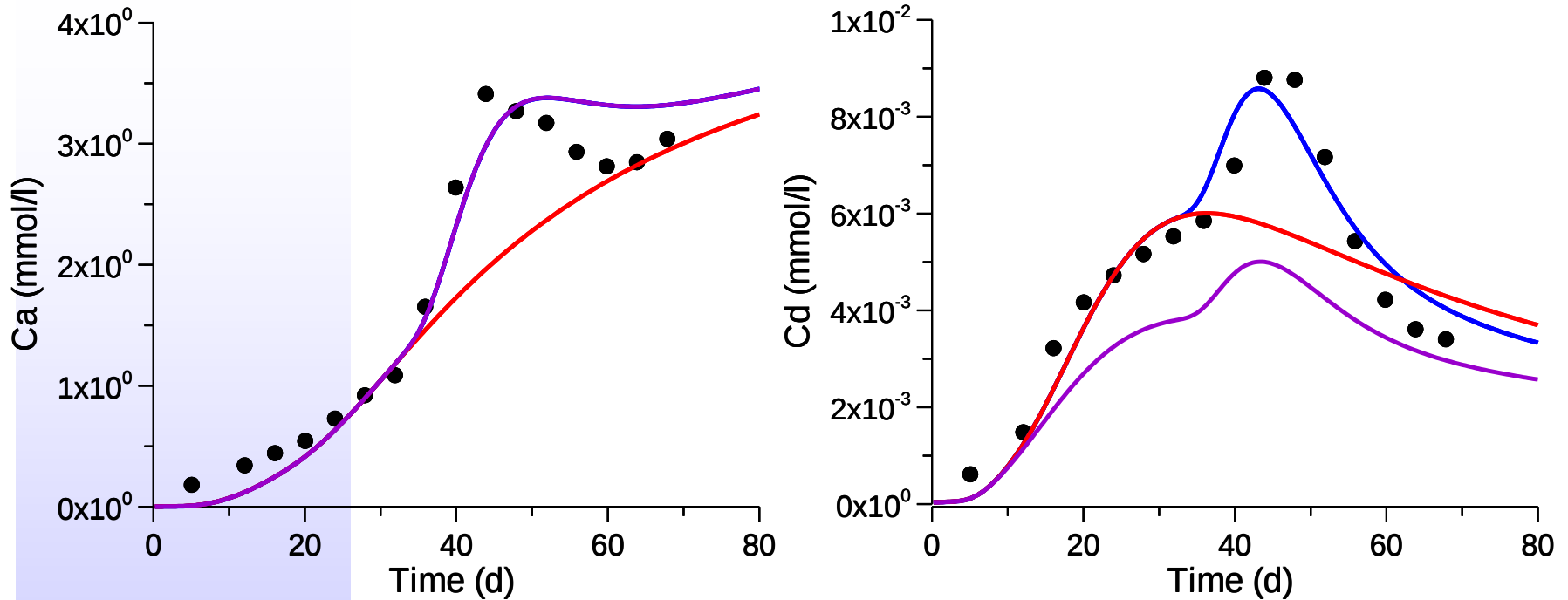
Time (d)	CaCl ₂ (mol/l)
0-27.9	0.005
27.9-28.9	0.05
28.9-80	0.005

Example: Cd leaching in a soil profile Breakthrough curves



— pulse 0.05 M CdCl₂ - complexation/competition

Example: Cd leaching in a soil profile Effect of composition of inflow



- pulse 0.05 M CdCl₂ - complexation/competition
- pulse 0.005 CaCl₂ - less complexation/competition
- pulse 0.05 CaBr₂ - competition (no complexation)

Example: Cd leaching in a soil profile Use in safety analysis deep disposal

- Relation complexation of radionuclides – mobility of radionuclides
 - ♣ Including: competition between complexation reactions
($\text{RNL}_{(\text{aq})}$ versus $\text{MeL}_{(\text{aq})}$)
- Alternative to single K_d or retardation factor approach for interpreting experiments
- Obtaining parameters with fitting procedures combining a geochemical model with a calibration/fitting program

Fully coupled models versus reaction path / geochemical models

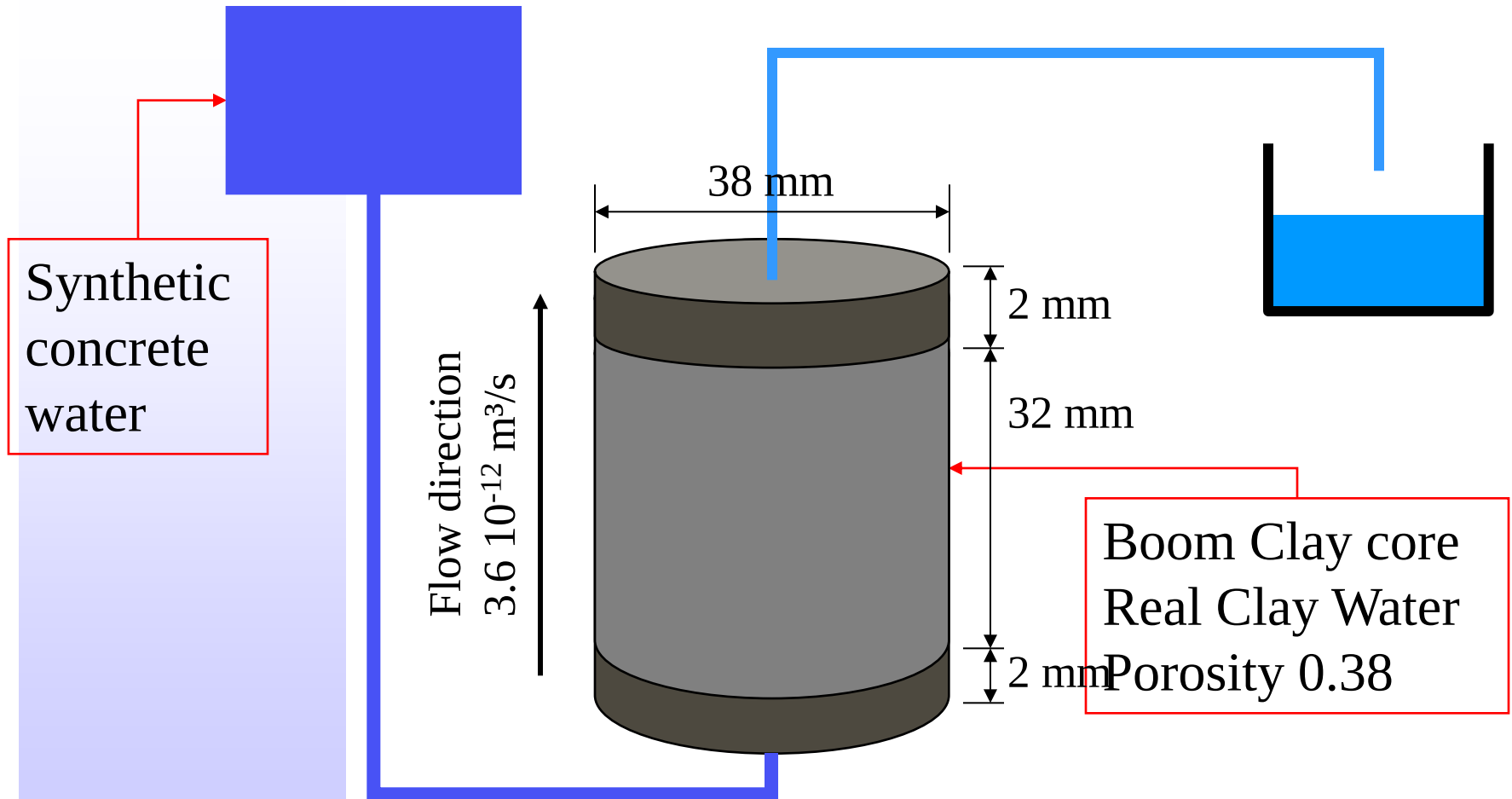
- Ability to incorporate diffusive and dispersive transport
- Chemical heterogeneities easily incorporated
- Relatively easily coupled to other time-dependent processes (e.g. heat transfer, evolving medium properties)
- Provides information on spatial distribution of processes

Alkaline fluid through Boom Clay

Problem definition

- Concrete liners are required for deep disposal in Boom Clay
- (Young) Concrete water: high pH, high Na and K concentrations
- Elements in concrete water will diffuse into the Boom Clay
 - => not in equilibrium with Boom Clay
 - => changing geochemical conditions in the near field

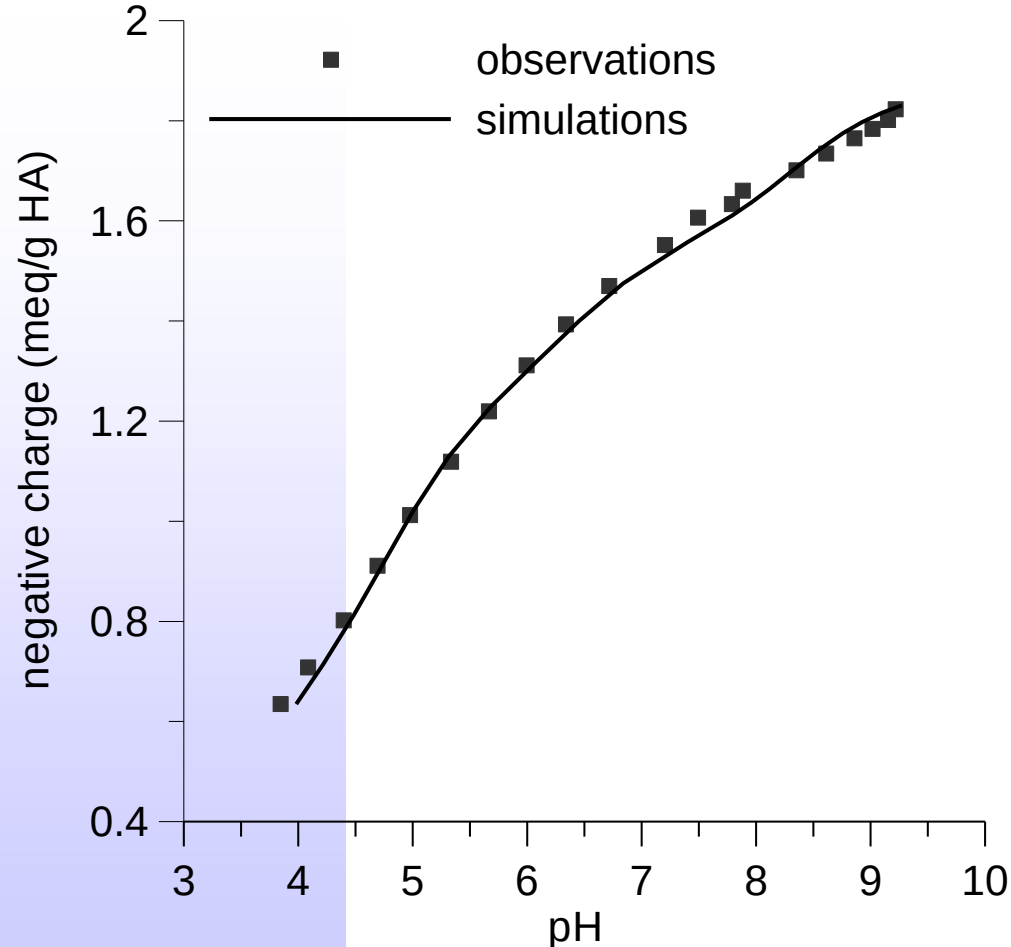
Alkaline fluid through Boom Clay Experimental set up



Alkaline fluid through Boom Clay Geochemical modelling

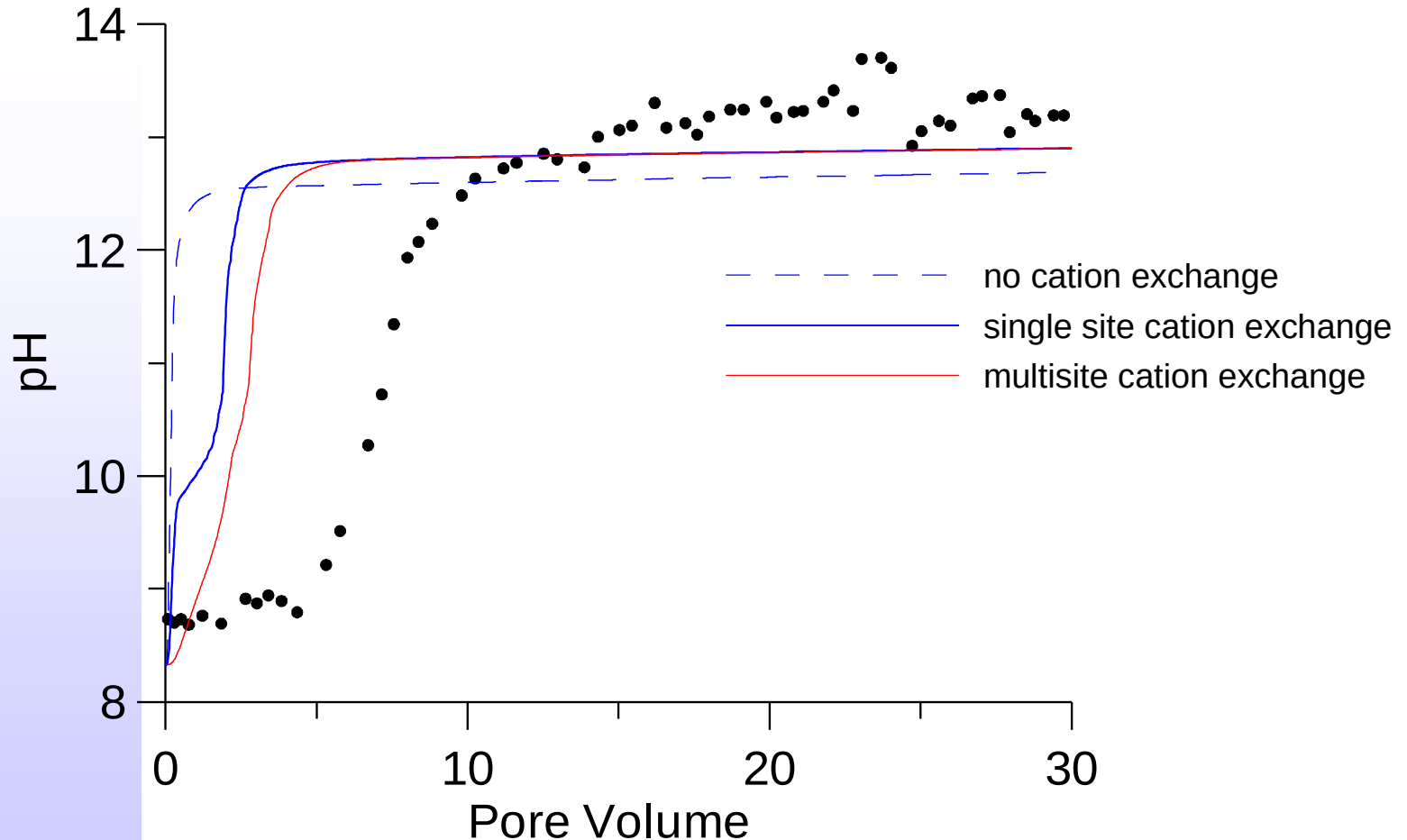
- Inflowing solution
 - pH 13.1; Na 1490 mg/l; K 5500 mg/l
- Primary minerals: kinetic precipitation/dissolution
 - Illite, monmorillonite-Na, kaolinite, microcline, quartz, albite, calcite
- Secondary minerals: equilibrium precipitation
 - CSH-phases, zeolites, sepiolite, ...
- Cation exchange processes (2 approaches):
 - Singlesite cation exchange without proton exchange
 - Multisite cation exchange including proton exchange

Alkaline fluid through Boom Clay Multisite cation exchange complex

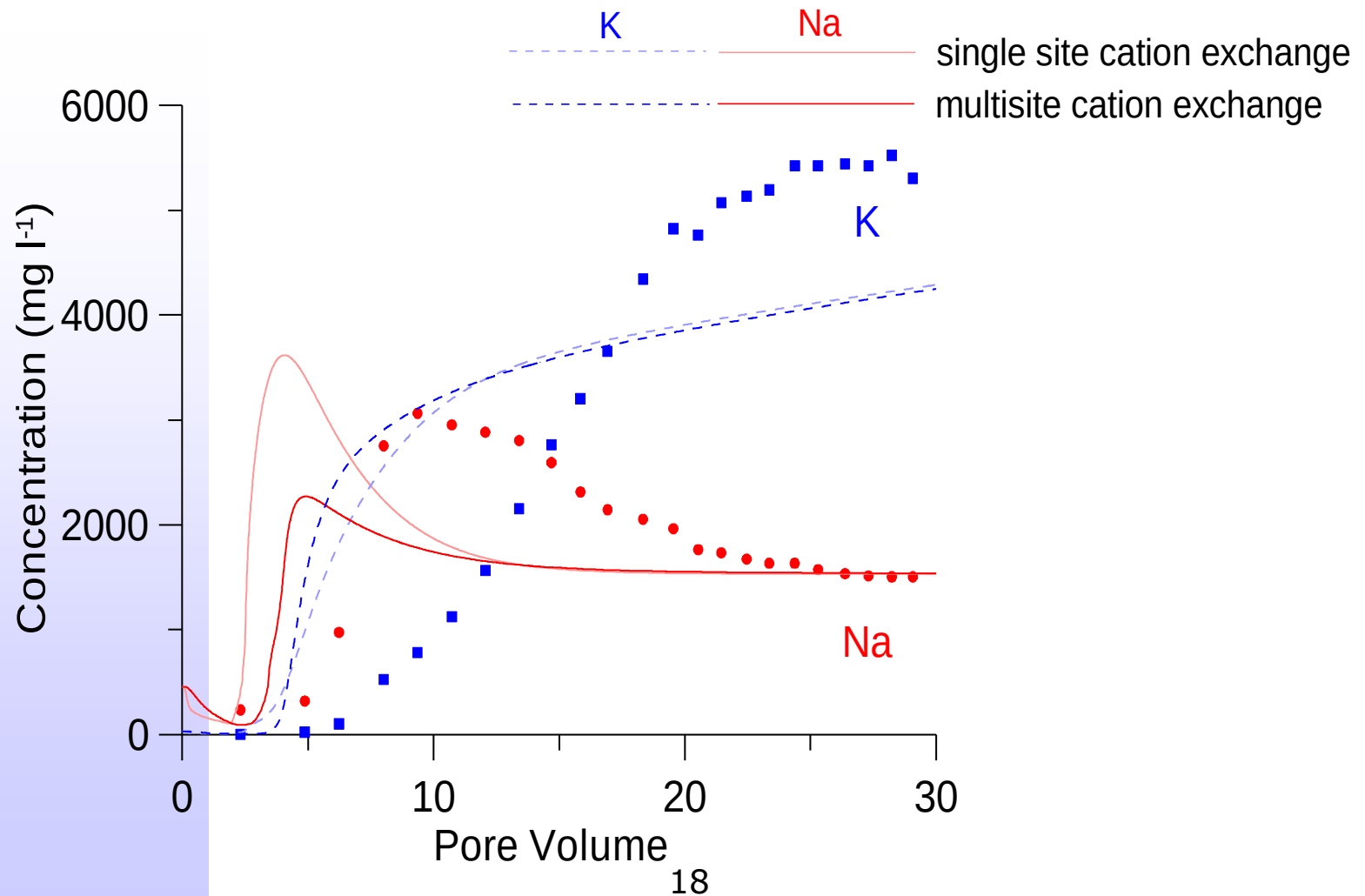


Site	Log_k
Ya	1.65
Yb	3.30
Yc	4.95
Yd	6.85
Ye	9.60
Yf	12.35

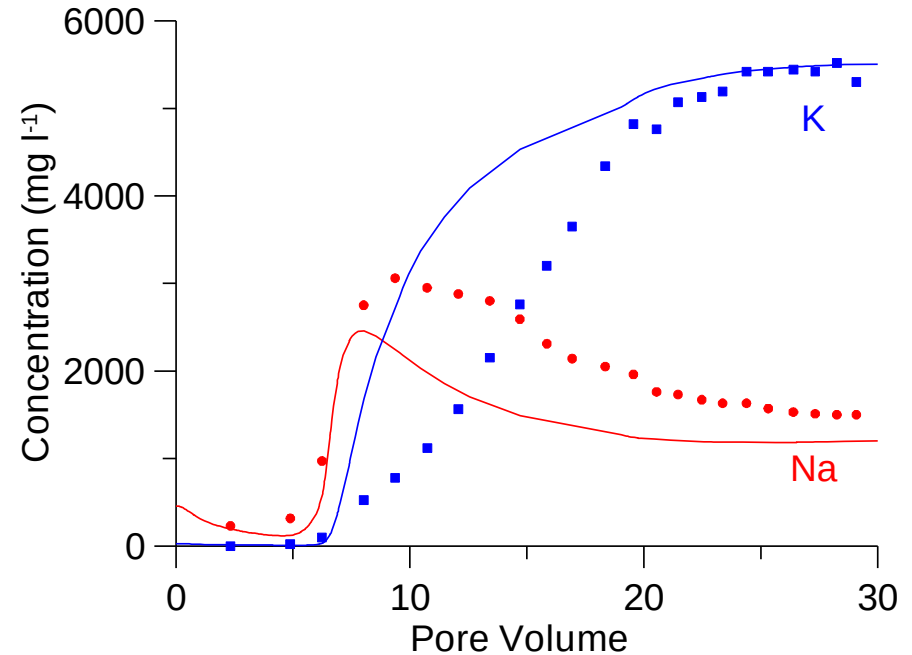
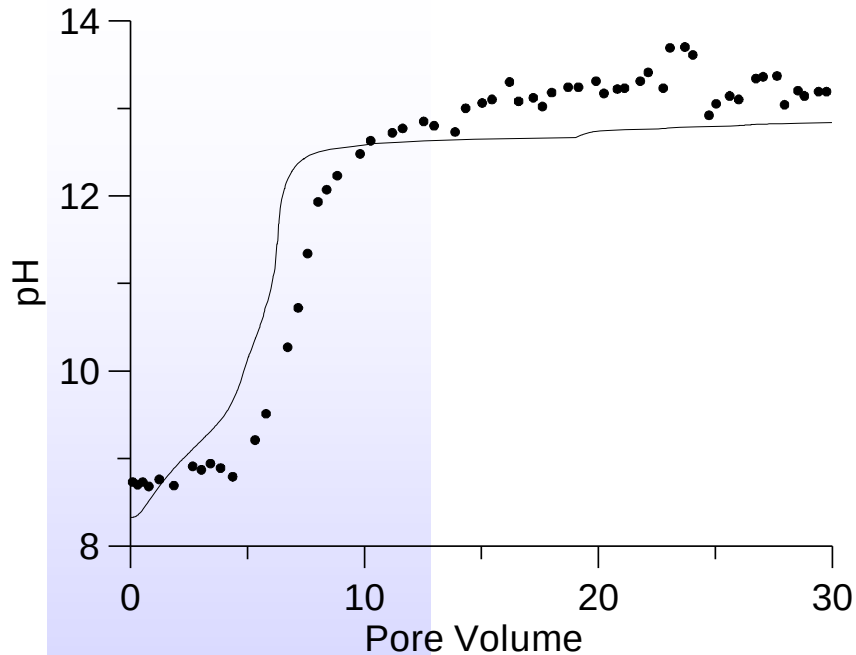
Alkaline fluid through Boom Clay Effect of cation exchange model



Alkaline fluid through Boom Clay Effect of cation exchange model



Alkaline fluid through Boom Clay No secondary K-phase



Alkaline fluid through Boom Clay Conclusions

- It is possible to model the experiments with young concrete water to reproduce the main features
- However, some agreements were poor, indicating that some mechanisms are more complicated than the ones considered in the geochemical model (e.g., interaction organic constituents – clay – solutes)

Applications of reactive transport modeling in deep geological disposal

- Which processes are determining the transport of RN through the Boom Clay observed during migration experiments?
- How do the geochemical conditions in different barriers change with time and how do the barriers interact with each other?
- How far will oxygen diffuse in Boom Clay and oxidize pyrite?
- Will heat (produced from the waste) influence the mobility of RN?

Available reactive transport codes at Waste and Disposal

- Geochemist Workbench
- Crunch
- PHREEQC
- HYDRUS1D-PHREEQC
 - 'in house' coupled model
 - Coupling with hydrology / water flow
 - Unsaturated / transient flow conditions
 - Interaction with atmosphere (precipitation / evaporation) and plants / biosphere
 - Typically applications: Soil

- Reactive transport modelling need a strong interaction with pure geochemical modelling:
 - Conceptual models
 - Parameters
- Reactive transport modelling enables to model the spatial zonation and temporal dynamics of different 'geochemical' domains
 - RN mobility

Geochemical reaction modeling: principles and applications

Lian Wang

- Model
 - A testable idea, hypothesis, theory
- Modeling
 - An action using a model to interpret and/or predict processes/phenomena
- Computer simulation
 - Modeling with computers

- Principles

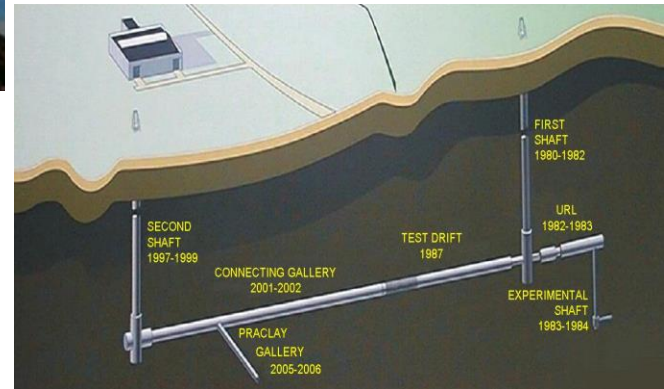
- Mass action and mass balance laws
- Speciation: the key to identify geochemical processes

- Applications

- Modeling Boom Clay pore water
- Modeling Boom Clay oxidation phenomena

Principles chemical thermodynamics

Energy



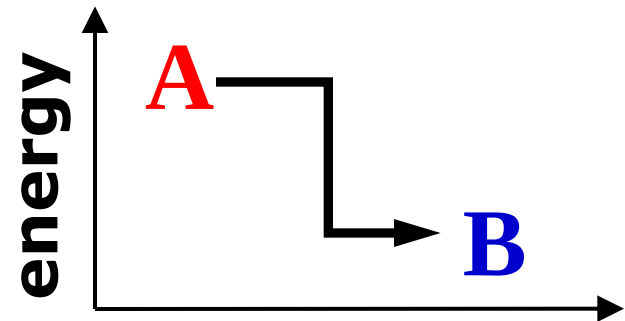
Principles: a system evolves spontaneously to a lower energy level

Oxidation of Boom Clay

- Pyrite (FeS_2) + H_2O + 3.5O_2 =
 2H^+ + 2SO_4^{2-} + Fe^{2+}
- System constraints
 - Mass action:

$$G^0 - G^0 = \Delta G^0 = -RT \ln K$$

- Mass balance



**Database: 1768 species, 1121 minerals, 93 gases,
 ion exchange, sorption, OM...**

Chemical speciation

- Speciation
the distribution of a chemical component among minerals, species, and gases
- A chemical component can exist in different forms and change from one to the other

Chromium "*Cr*": Cr(III) nutrient, Cr(VI) toxic

Speciation: the key to identify geochemical processes

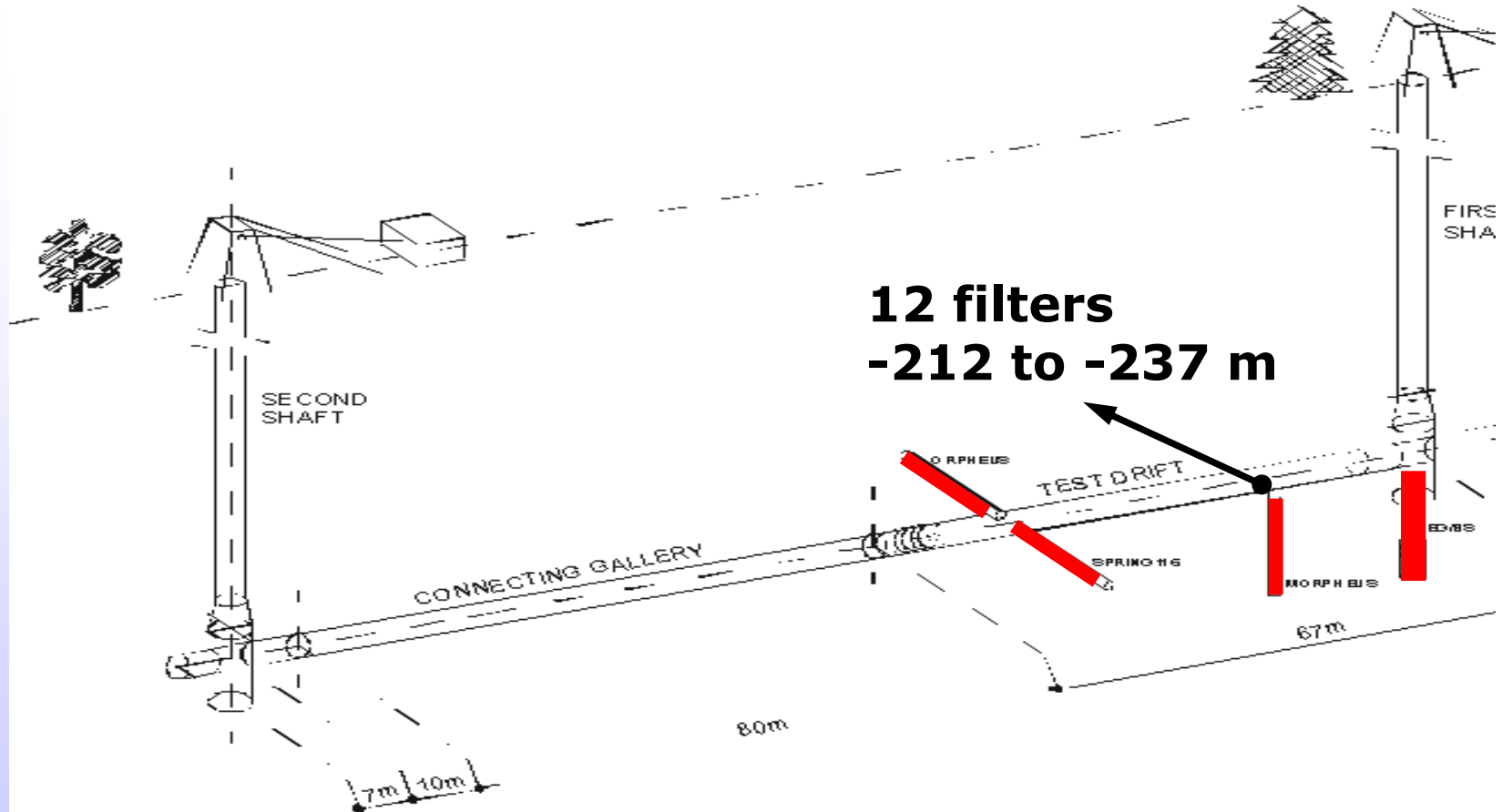
Clay dissolution by an alkaline plume

- $\text{Smet} + 4.68\text{OH}^- = 1.34\text{H}_2\text{O} + .33\text{Mg}^{2+} + .33\text{Na}^+ + 1.67\text{AlO}_2^- + 4\text{HSiO}_3^-$
- $\text{Smet} + .62\text{H}_2\text{O} + .68\text{OH}^- + 1.5\text{Na}^+ + .21\text{AlO}_2^- = .33\text{Mg}^{2+} + 1.961\text{Analcime}$
- Nature is a highly coupled, non-linear system...
- Certain level of understanding...

Application (1): Boom Clay reference model

- To understand the present-day BC composition by studying the mineralogy and the pore water composition and their interrelationships
- The start point for:
 - Modeling the BC evolutions
 - Predict the effects of perturbations
 - Chemical conditions for experiments

BC reference model: pore water sampling



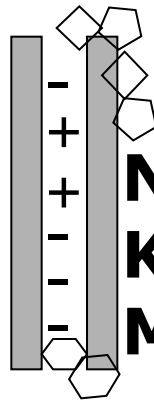
BC reference model: variations in concentrations

- Major ions:
 - Na: 348~431 mg/l
 - Ca: 1.5~2.9
 - K: 6.7~8.3
 - Mg: 1.3~2.6
 - Fe: 0.1~0.7
 - SO₄: 0.6~2.3
 - TIC: 173~206, pH ~8.2 (lab.), pCO₂ ?
- Trace ion:
 - Sr: 30 ppb ~ 30 ppm

BC reference model: plausible interpretations

the driving force: $\text{Calcite} + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-$

Boom Clay



Na⁺
K⁺
Mg²⁺

$\text{Na}^+ \text{K}^+ \text{Mg}^{2+}$

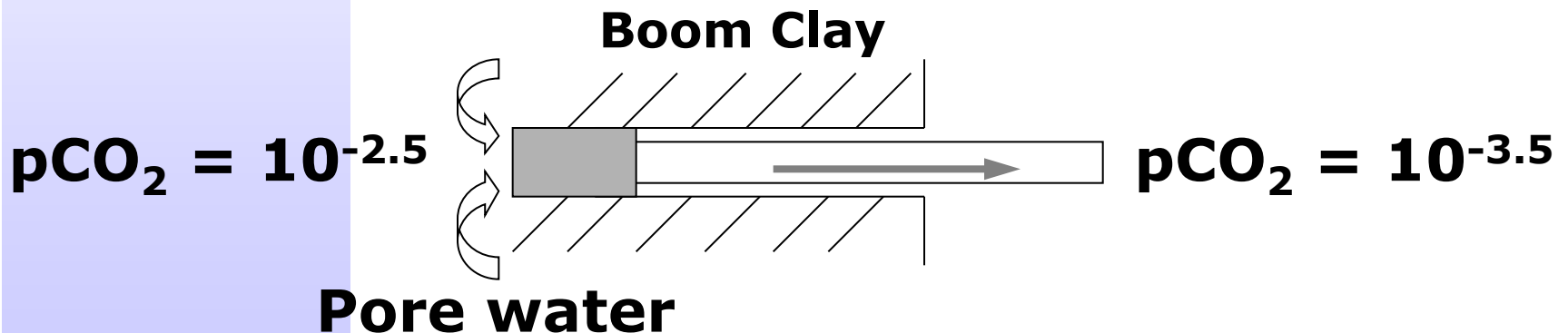
$\text{siderite} + \text{H}^+ = \text{Fe}^{2+} + \text{HCO}_3^-$

$\text{Pyrite} + \text{H}_2\text{O} + 3.5 \text{O}_2 = \text{Fe}^{2+} + 2 \text{H}^+ + 2 \text{SO}_4^{2-}$

BC reference model: why the solubility of calcite vary?



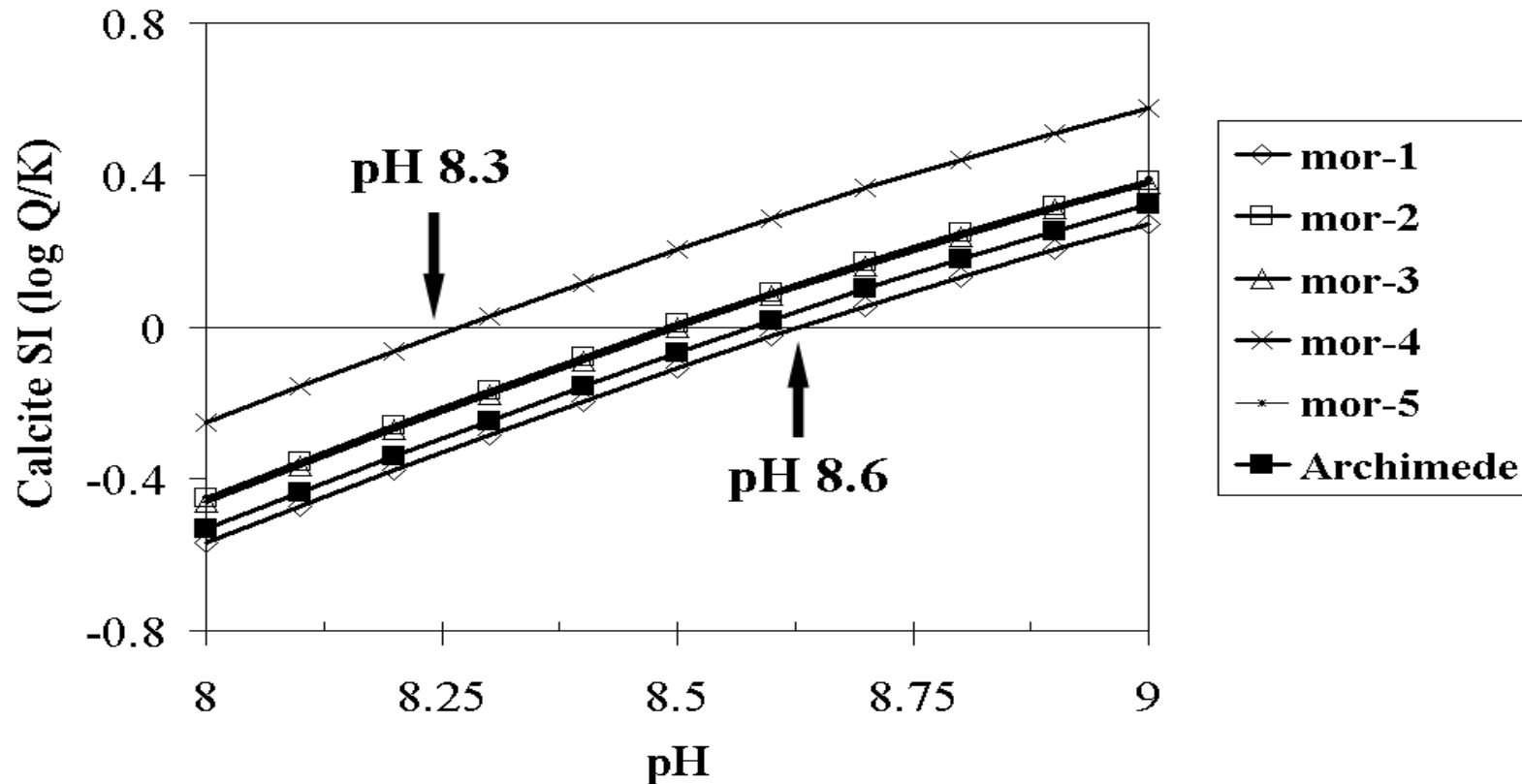
- pH variation is likely the cause
- However, pH is related pCO_2 and difficult to measure
 - $\text{H}^+ + \text{HCO}_3^- = \text{CO}_2 (\text{g}) + \text{H}_2\text{O}$



BC reference model: calculate the pH based on measured water compositions

Constraints: Calcite (CaCO_3) saturation: $\text{SI} = 0$

Alkalinity: conservative quantity

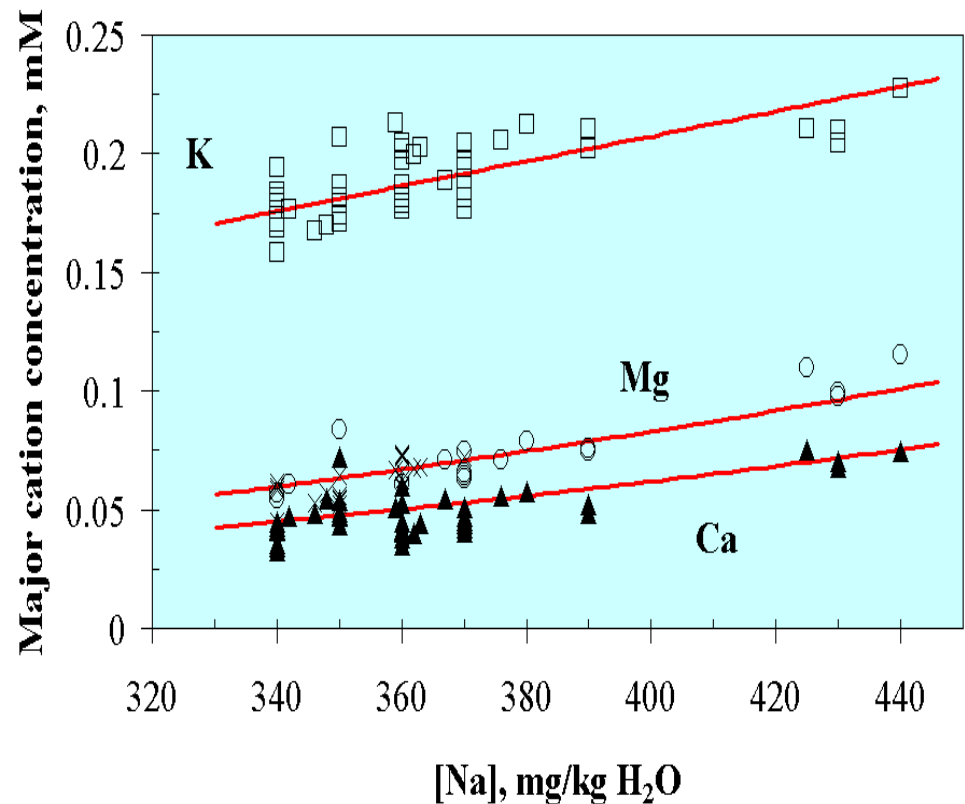


BC reference model: results (1)

- **System variable:**
 - **pH 8.3 to 8.6**
- **Ca: calcite solu.**

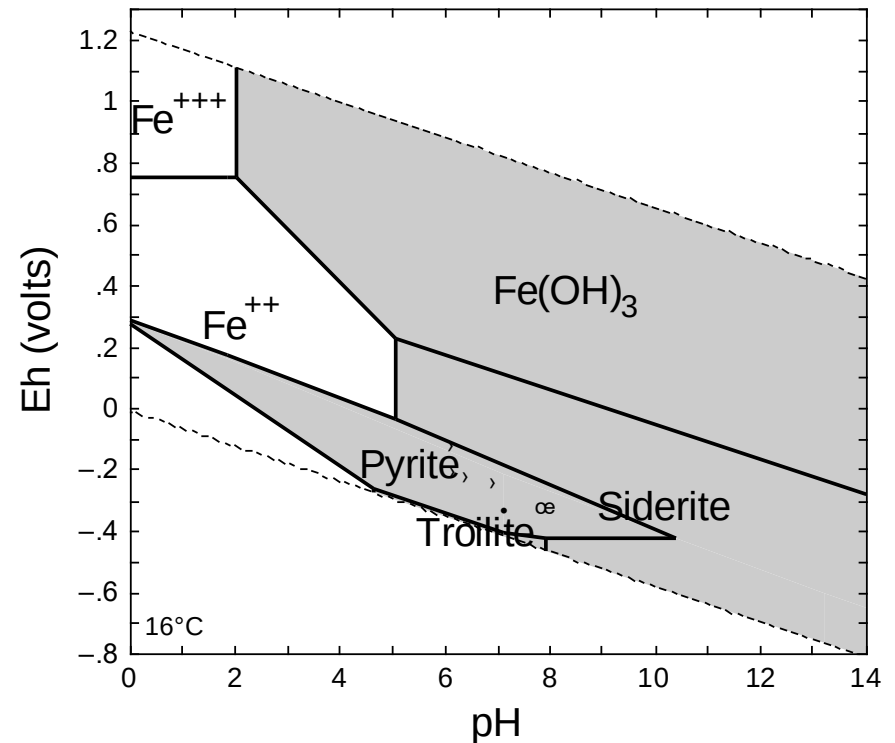
$$\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-$$
- **Na, K, Mg: ion exchange, e.g.,**

$$\text{clay-Mg} + \text{Ca}^{2+} = \text{clay-Ca} + \text{Mg}^{2+}$$

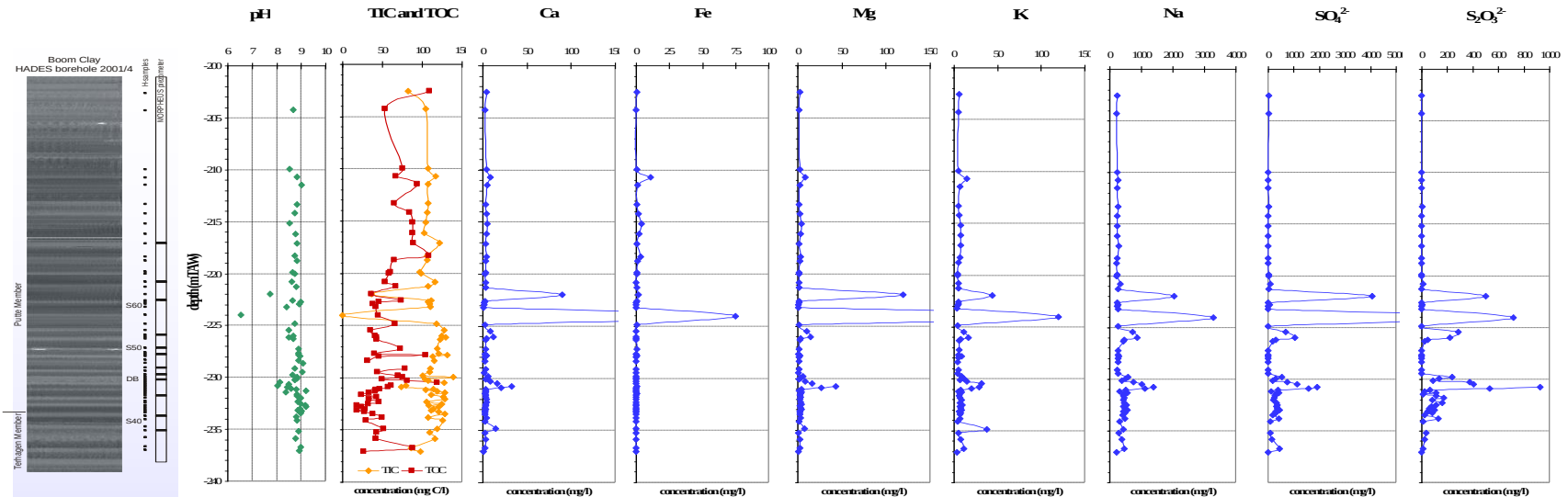


BC reference model: results (2)

- **Boom Clay redox is controlled by the pyrite-siderite boundary**
- **$Eh < -270$ mV for non disturbed clay**



Application: Oxidation of BC



- Some water samples have 10 to 20 kppm sulphate comparing to 1 ppm normally found in non-disturbed Boom Clay;
- Can the observation be explained?
- Excellent dataset to verify the BC reference model

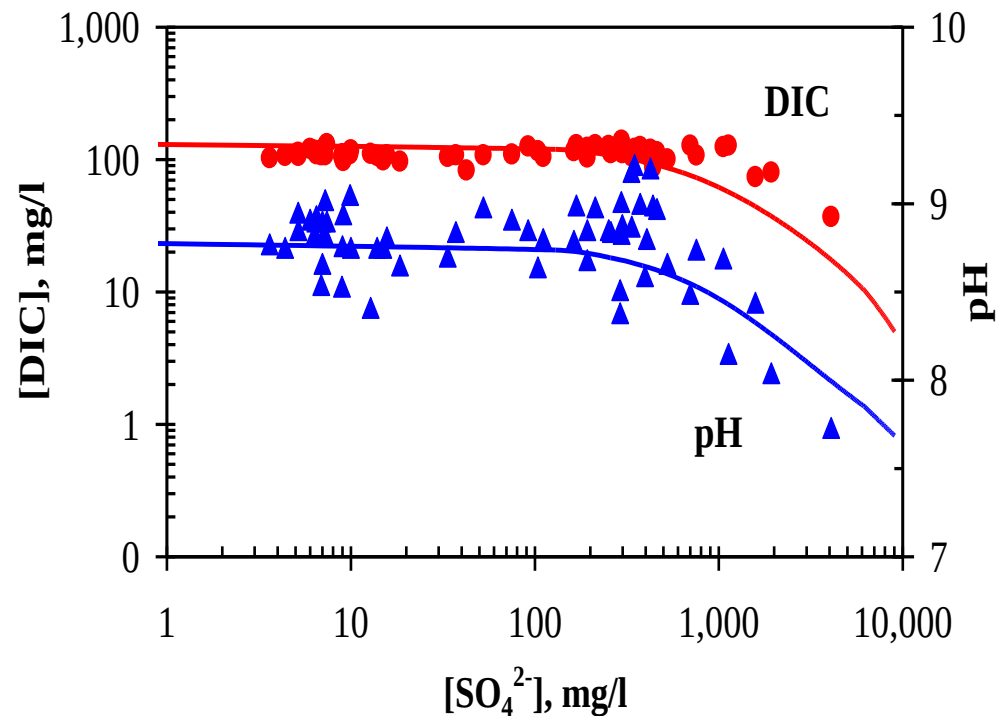
Application: Oxidation of BC

Possible processes

- $\text{Pyrite} + \text{H}_2\text{O} + 3.5 \text{O}_2 =$
 $2\text{H}^+ + 2\text{SO}_4^{2-} + \text{Fe}^{2+}$
- Calcite dissolves due to the decreased $p\text{H}$:
 $\text{Calcite} + 2\text{H}^+ = \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$
- Ca exchange Na, K, Mg from clay;
- Siderite (Fe) and Chalcedony (Si) dissolution

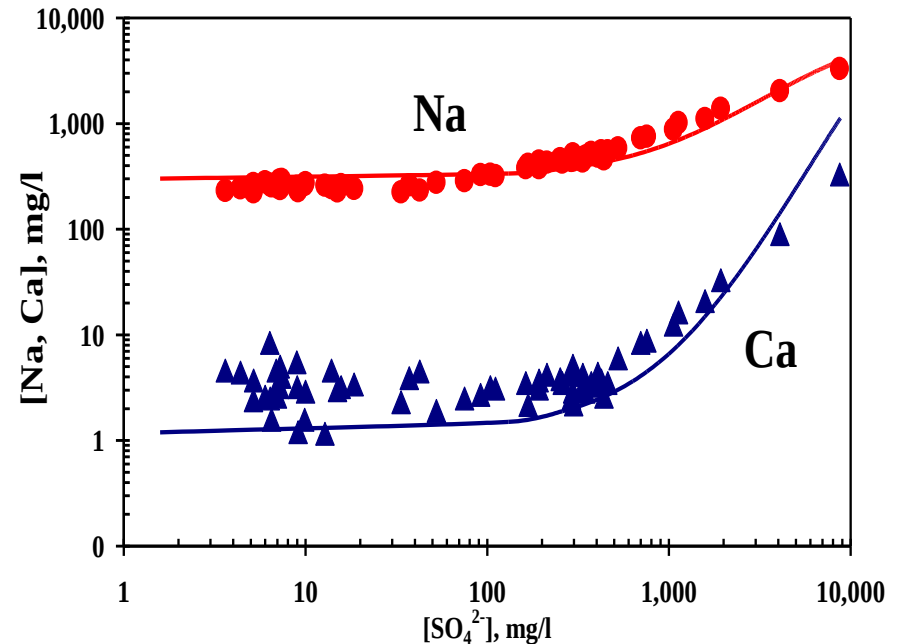
application: Oxidation of BC Model simulation on pH and DIC

- $p\text{CO}_2$ is a variable considering a partly open system;
- pH drops due to the oxidation of pyrite



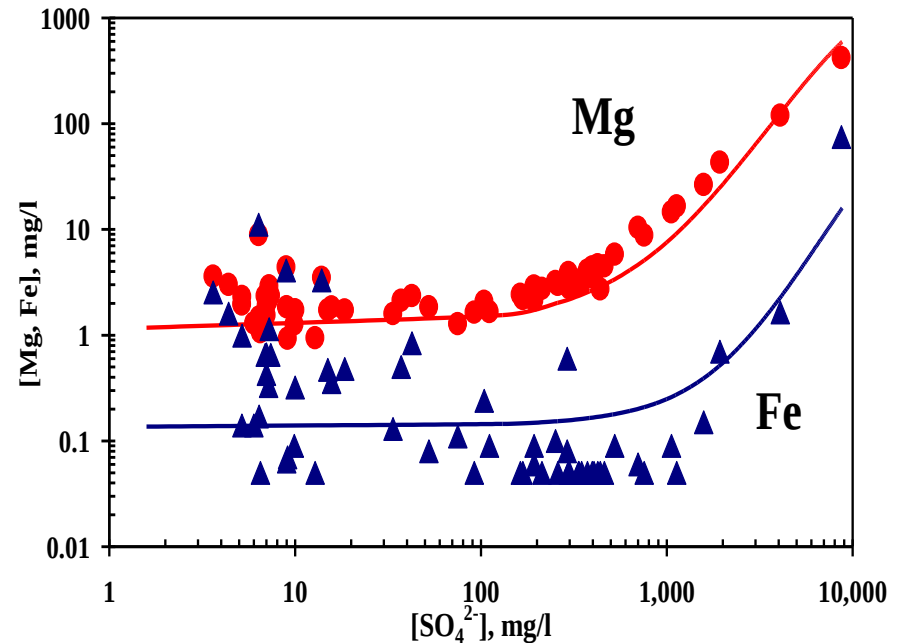
application: Oxidation of BC Model simulation on Ca and Na

- $\text{Pyrite} + \text{H}_2\text{O} + 3.5 \text{ O}_2 = 2\text{H}^+ + 2\text{SO}_4^{2-} + \text{Fe}^{2+}$
- $\text{Calcite} + 2\text{H}^+ = \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O};$
- $\text{Clay-Na} + \text{Ca}^{2+} = \text{Clay-Ca} + \text{Na}^+$



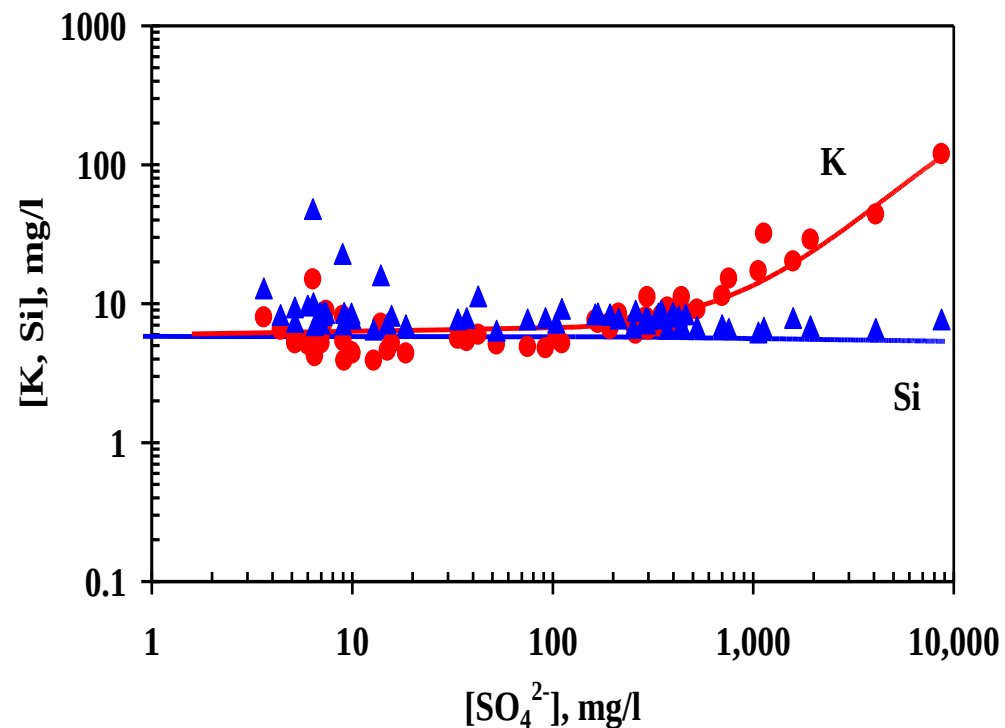
Application: Oxidation of BC Model simulation on Mg and Fe

- $\text{Clay-Mg} + \text{Ca}^{2+} = \text{Clay-Ca} + \text{Mg}^{2+}$
- $\text{Siderite} + \text{H}^+ = \text{Fe}^{2+} + \text{HCO}_3^-$



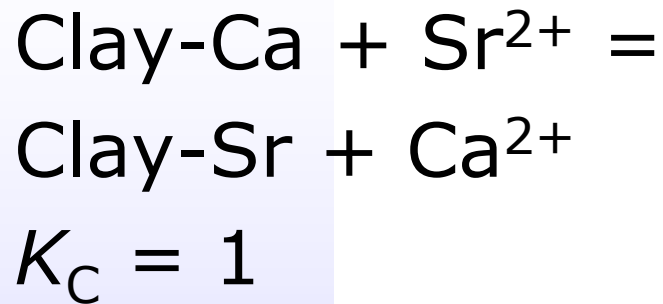
Application: Oxidation of BC Model simulation on K and Si

- $\text{Clay-K} + \text{Ca}^{2+} = \text{Clay-Ca} + \text{K}^+$
- $\text{Chalcedony} = \text{SiO}_2(\text{aq})$

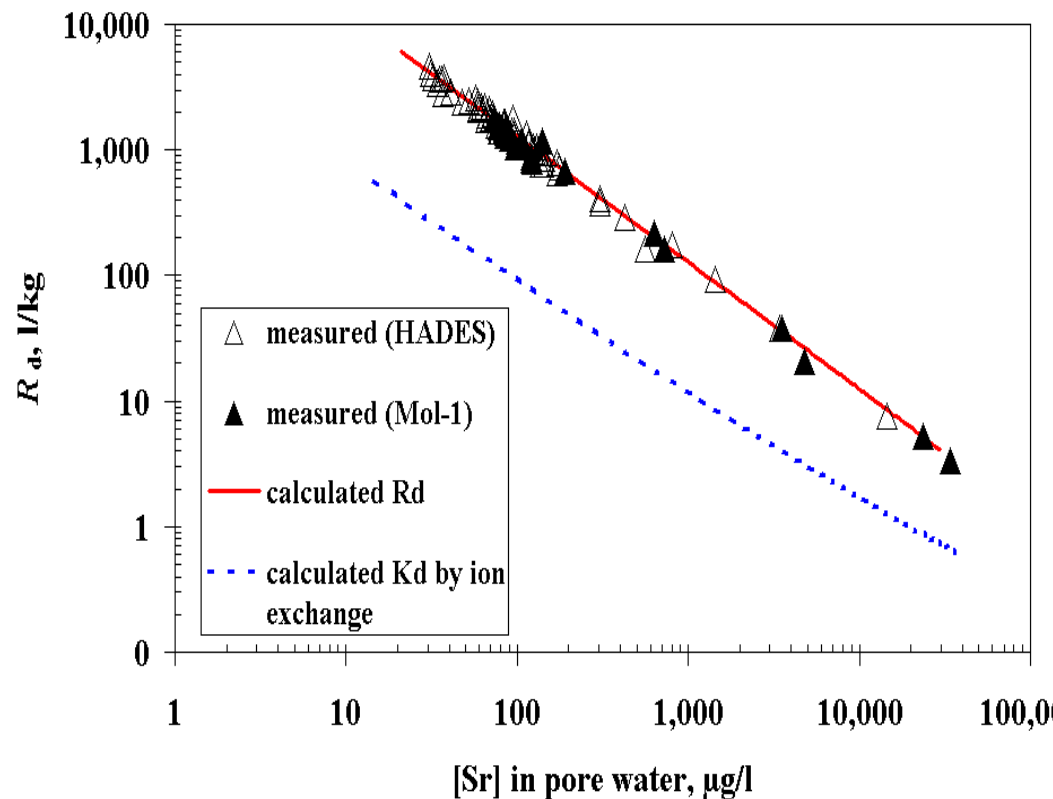
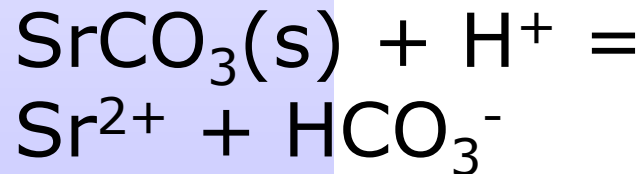


Application: Oxidation of BC Sr distribution (trace RN)

- Not a sorption

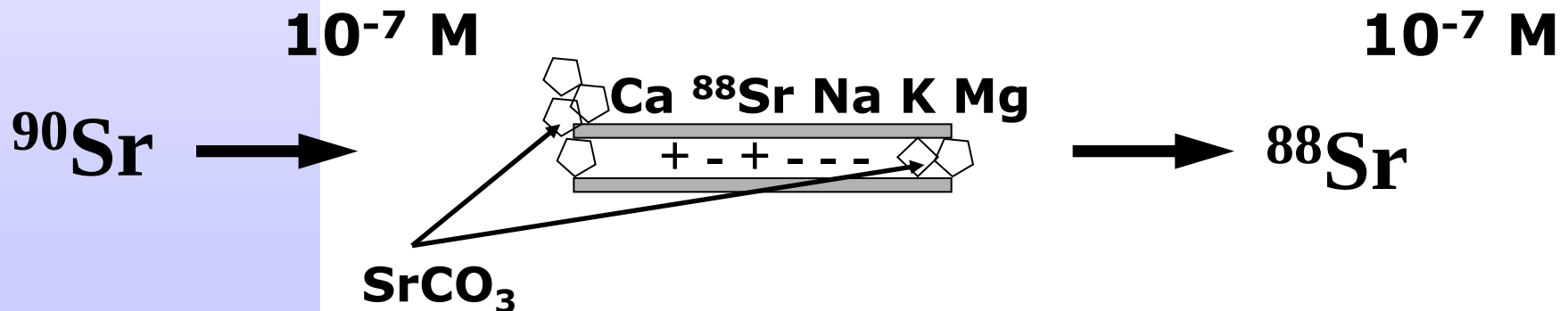


- But a solubility



Sr distribution: message to PA

- use a linear, reversible K_d model will underestimate the reduction on the safety caused by the oxidation of BC
- When a solubility controlling phase is present, the retardation of RN is controlled by isotopic exchange, not sorption



Mathematics and thermodynamics deal with models of reality, not with reality itself

G.M. Anderson & D.A. Crerar

Geochemical simulation on OPHELIE mock-up

Diane Sali

This work is part of a collaboration between NIRAS/ONDRAF and Andra in the framework of the EIG EURIDICE

Follow up of the study :

N. Michau – Andra

H. Van Humbeeck – EURIDICE

P. De Cannière – SCK-CEN

B.Fritz – CNRS-CGS Strasbourg (scientific support)



ESV EURIDICE GIE

OPHELIE acronym of ...



- On surface Preliminary Heating simulation
Experimenting Later Instruments and Equipments



● Technical experiment:

- to test instruments and equipments
- to test the installation procedures of the backfill blocks and the instruments
- to tune the hydration and the heating phases

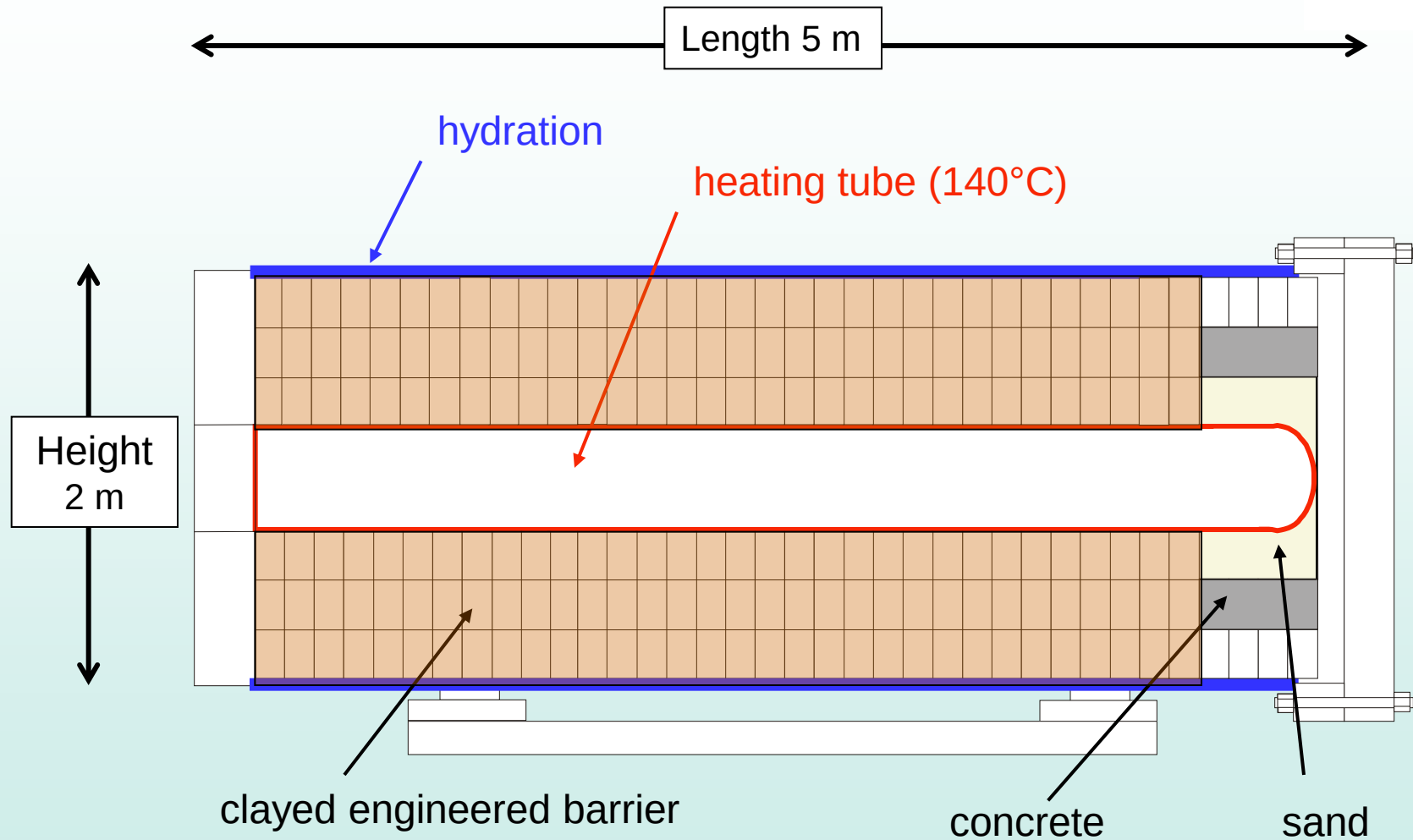
● To study the THMC behaviour of the backfill material on real scale

● The mock-up is integrated in the permanent exhibition on the HLW disposal concept

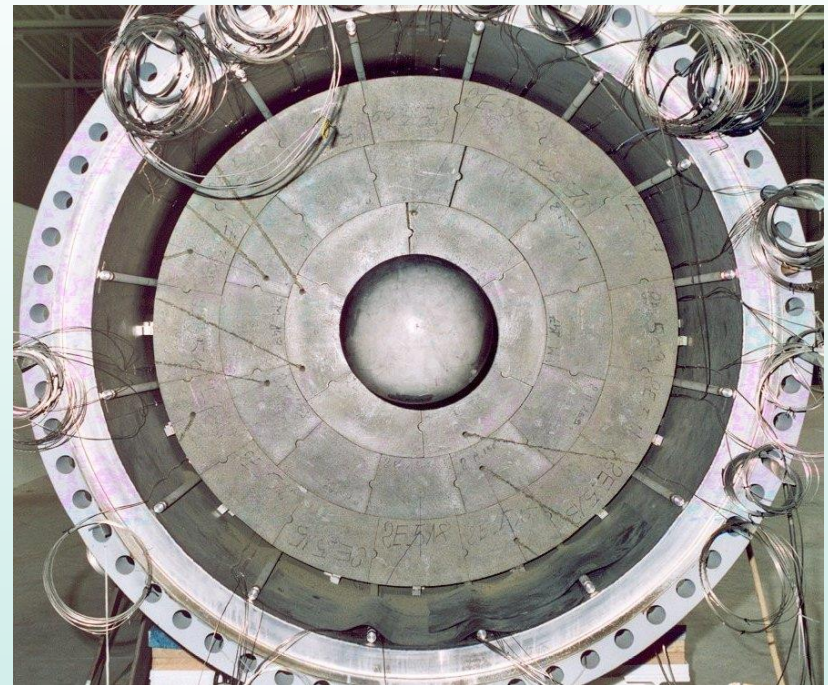
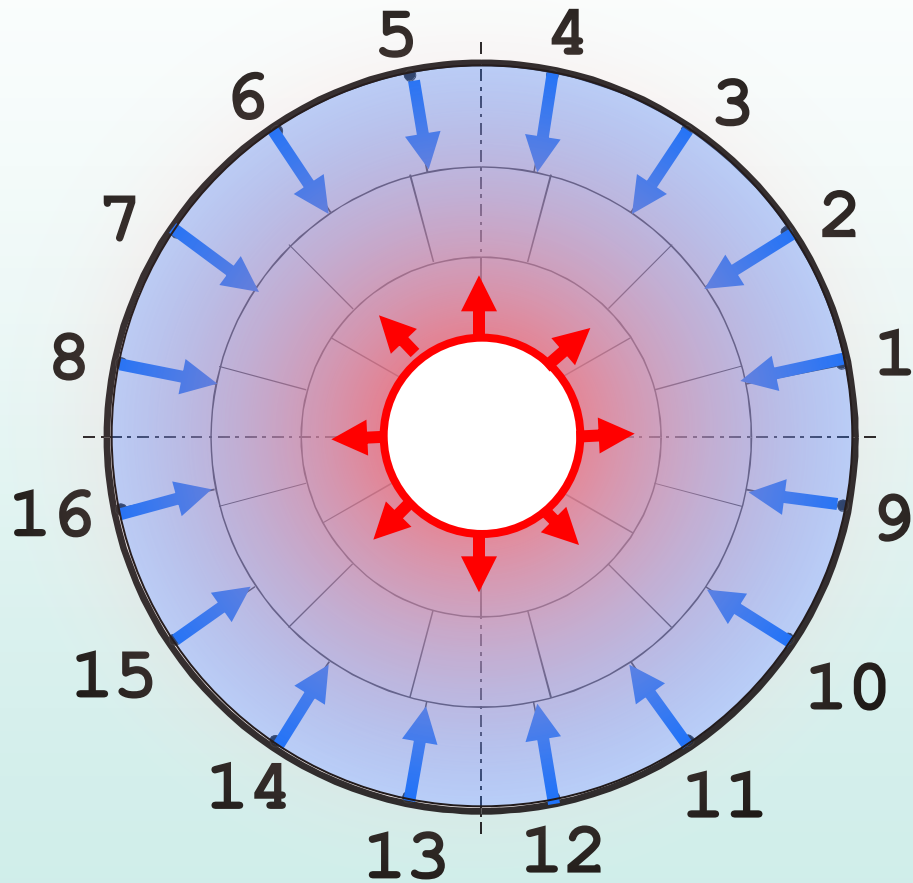


ESR EURIDICE GIE

Mock-up design

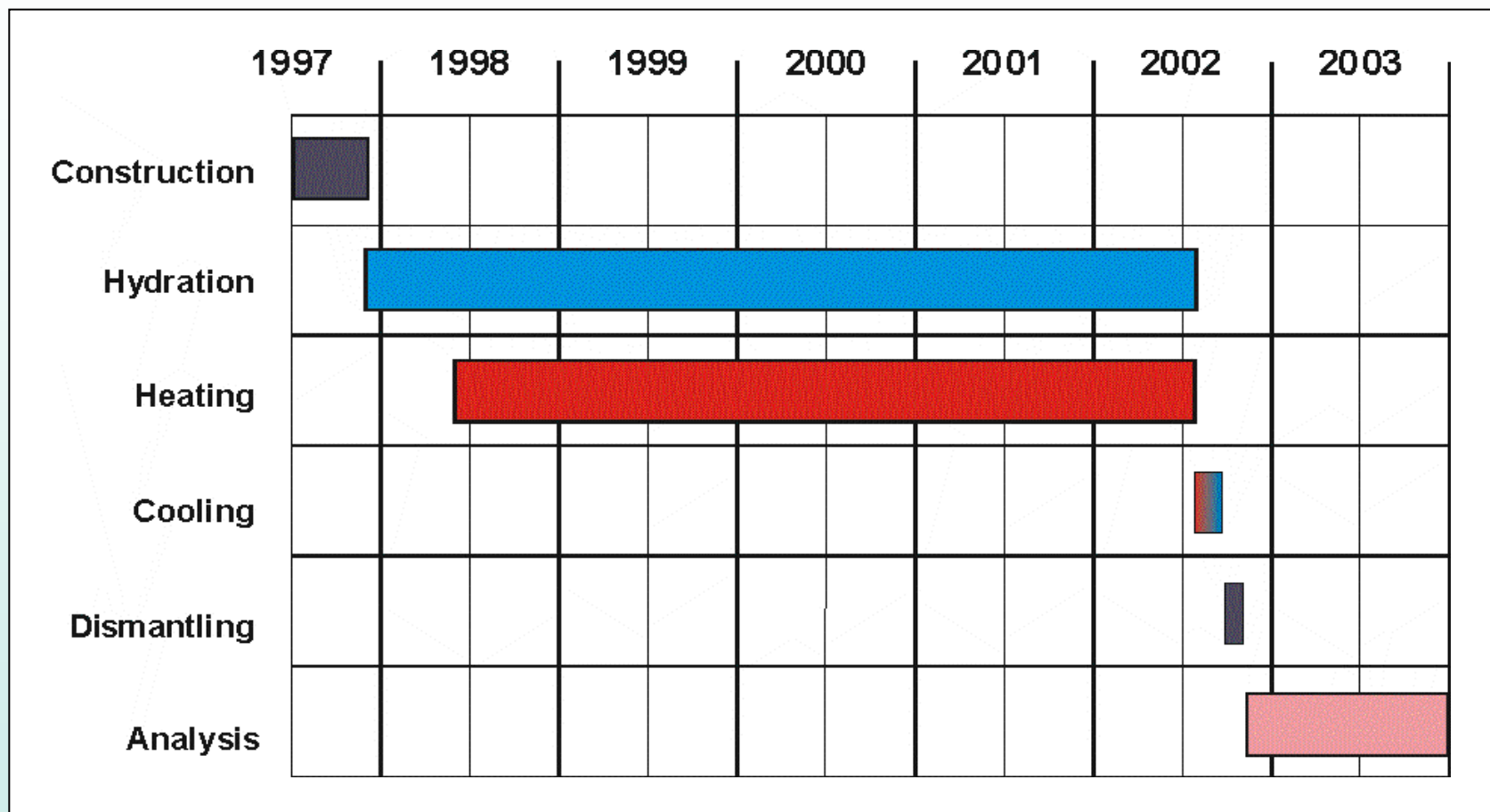


Design based on the HLW disposal concept of the 1990s





Planning of the mock-up

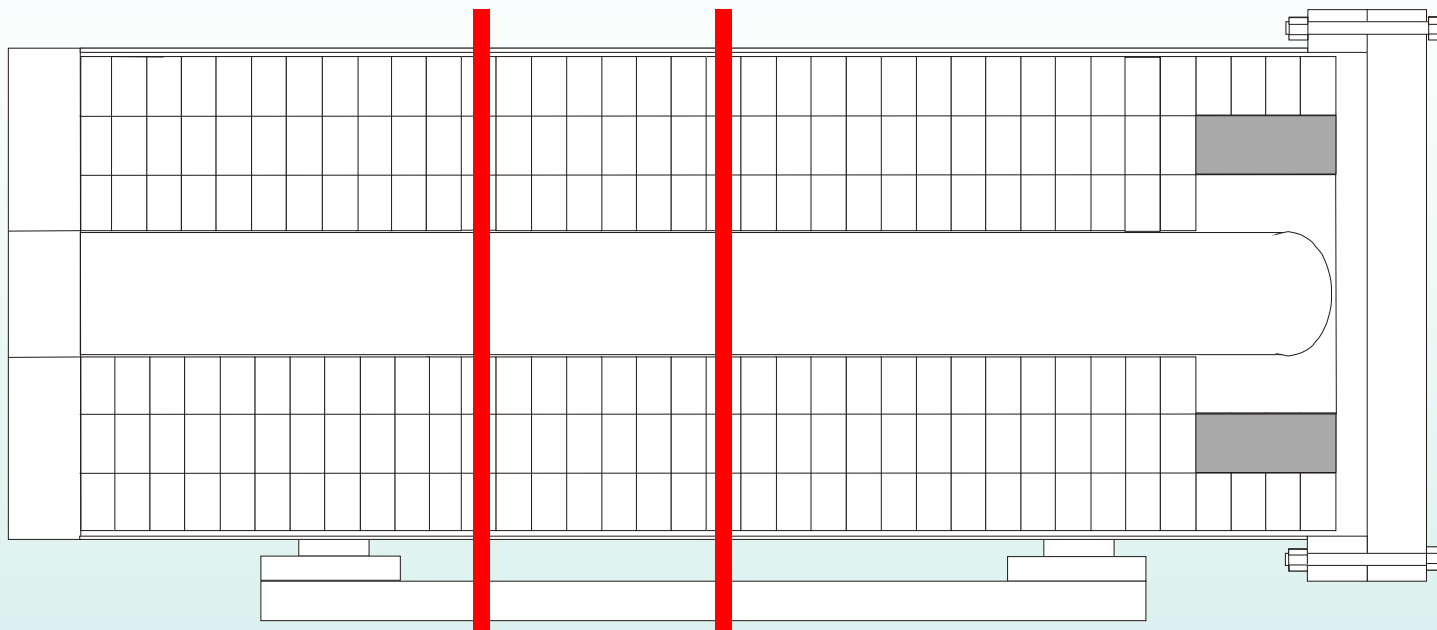




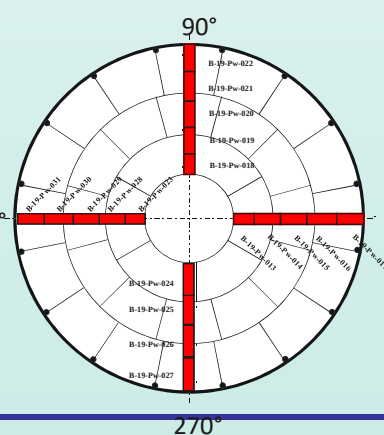
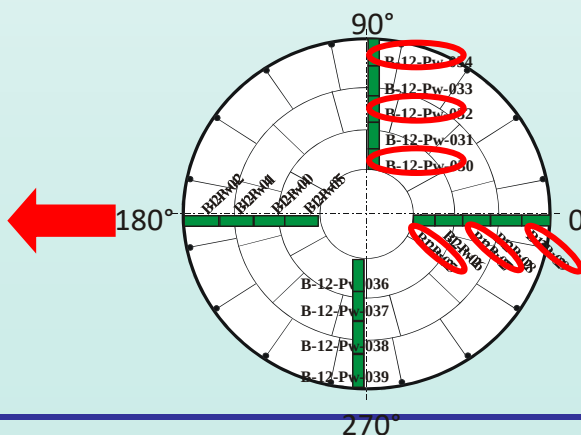
Dismantling main analytical results

SECTION 12

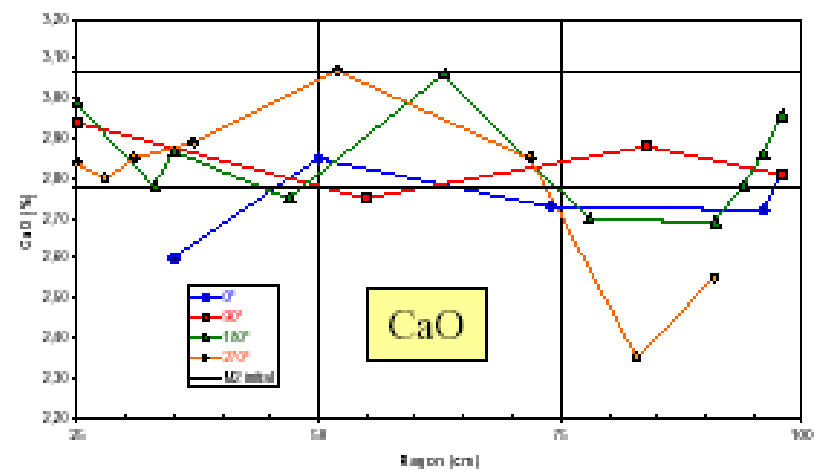
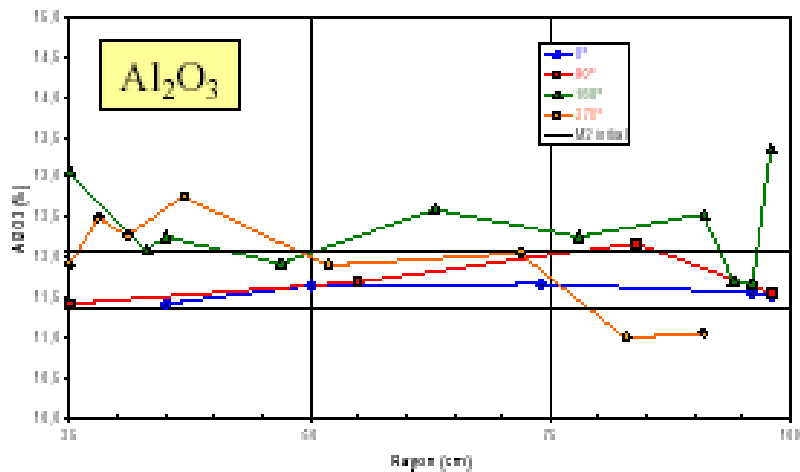
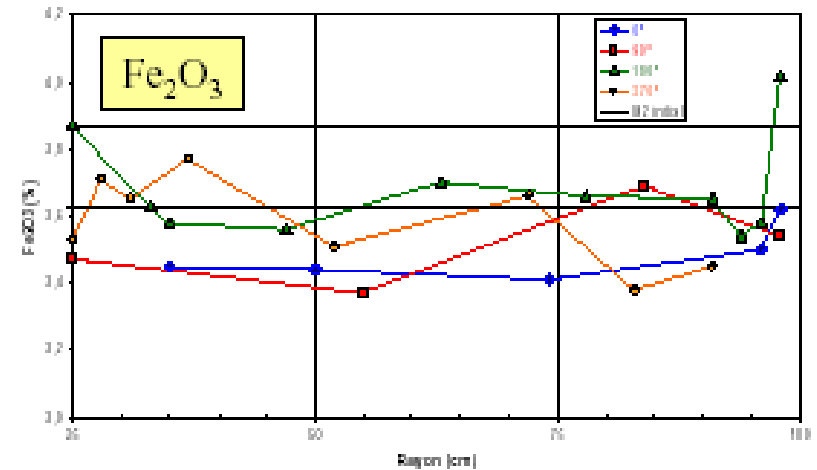
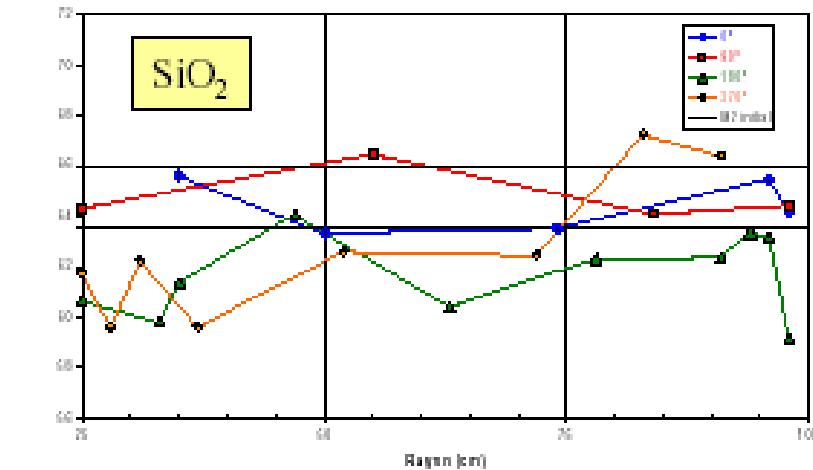
SECTION 19



Additional
analysis



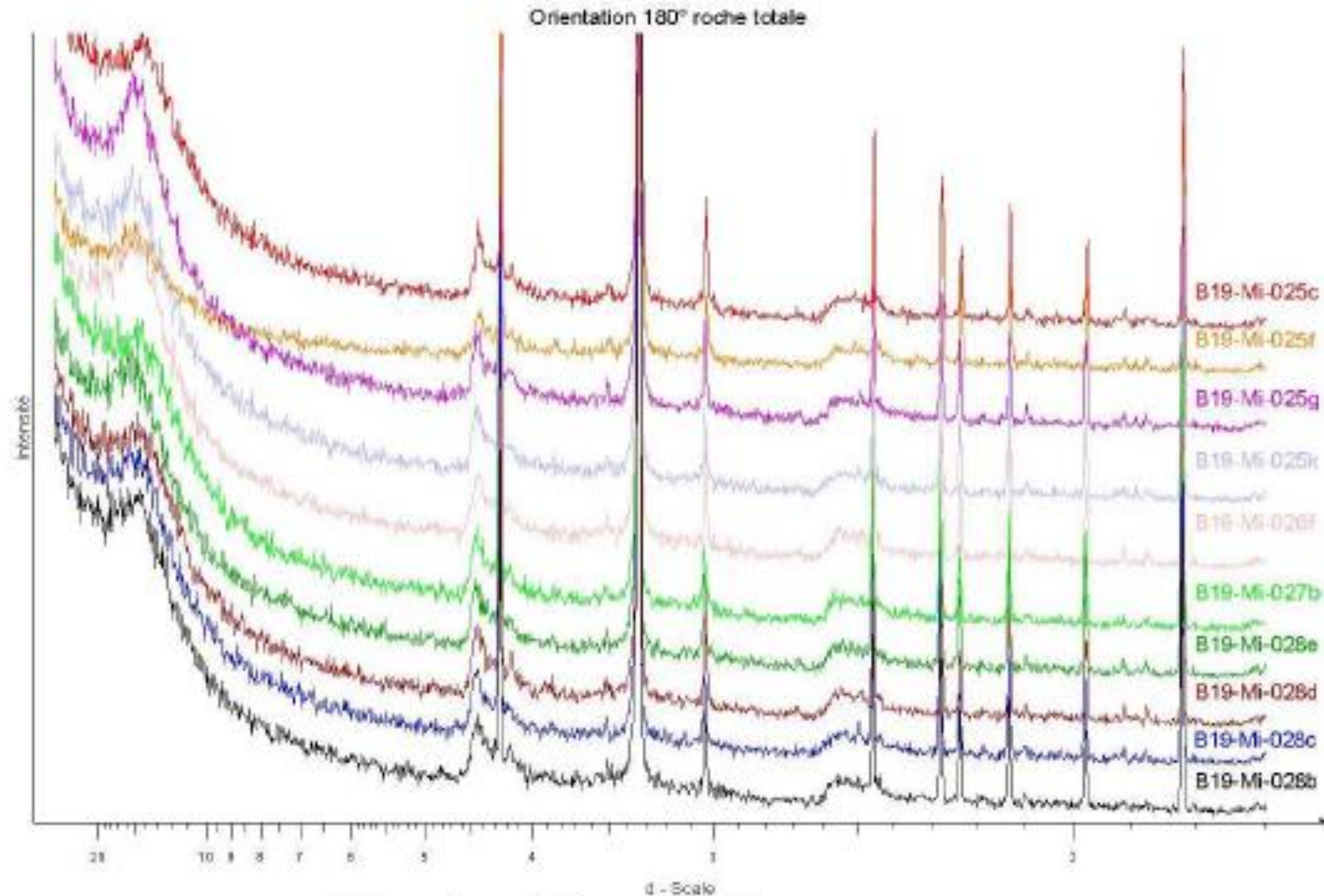
Whole profiles



No significant change



X Ray Diffraction



No significant change



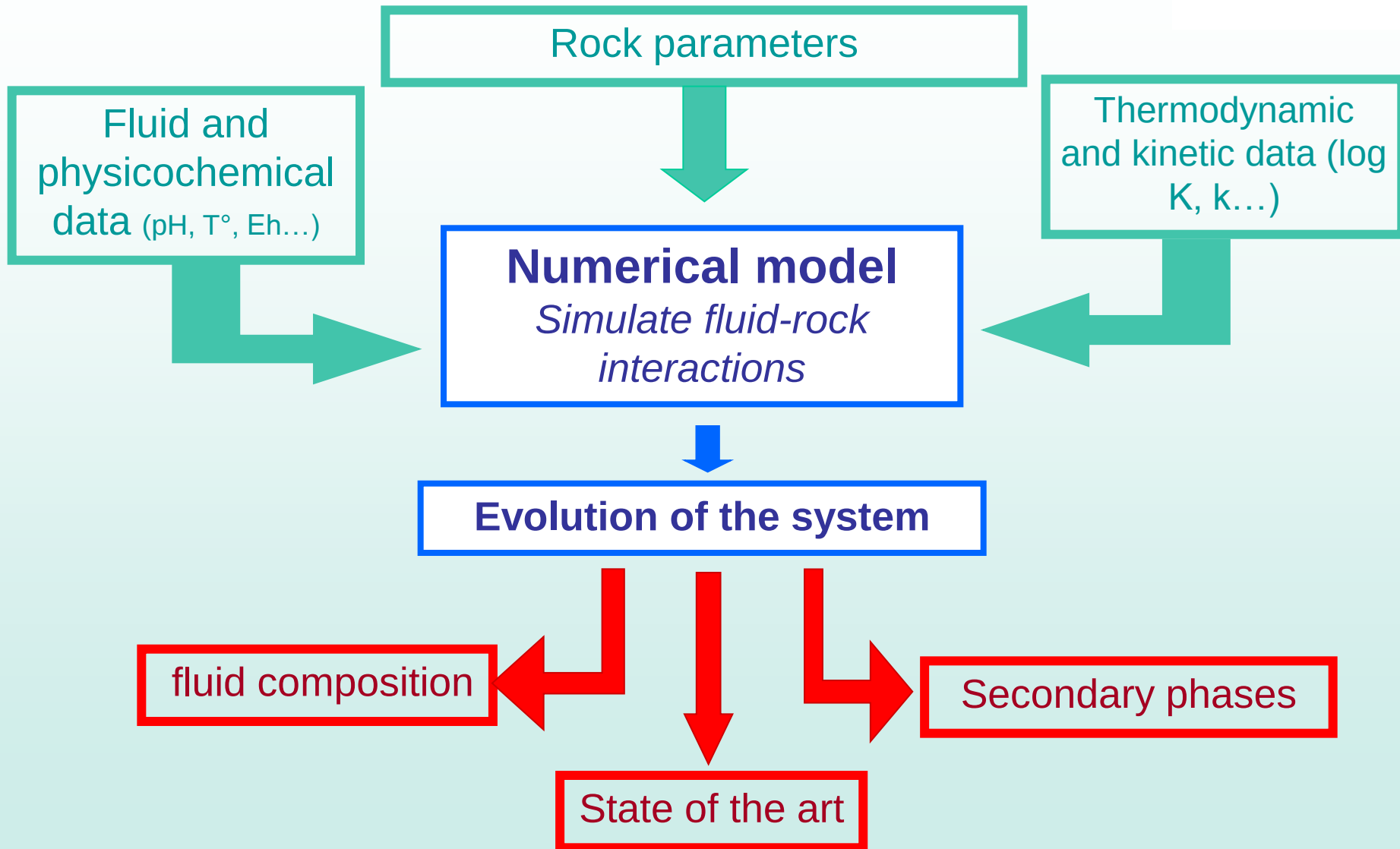
What happened in the mock-up ?

From the results of analytical analysis, it seems nothing chemically happened in the mock-up. Nevertheless some questions remain:

- which processes occurred in the mock-up to explain this strong stability ?
 - Can we assume the stability will remain on the long term ?
 - OPHELIE is an on-surface experiment in oxidizing conditions. What would happen if the system was in underground reducing conditions?
-

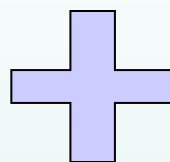
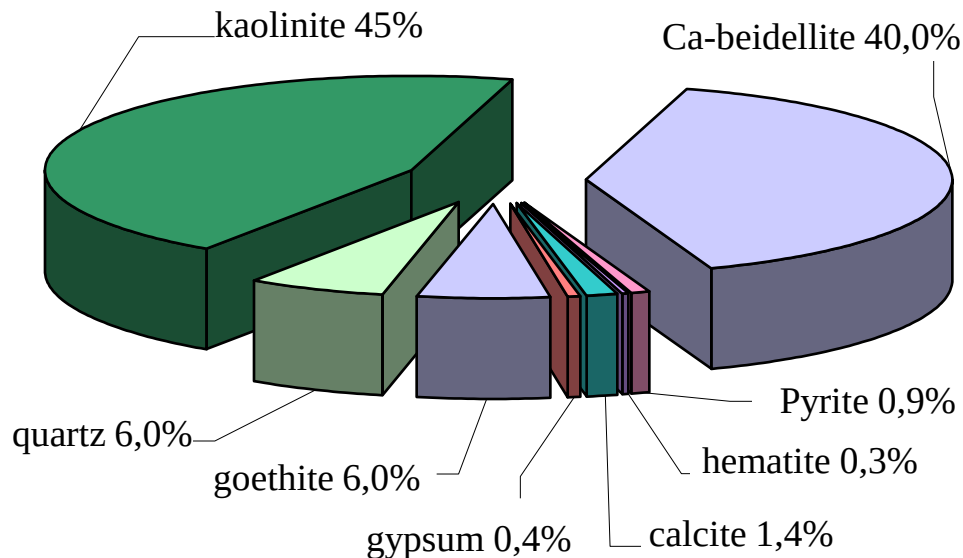


Modelling rock-fluid interactions



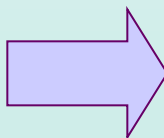
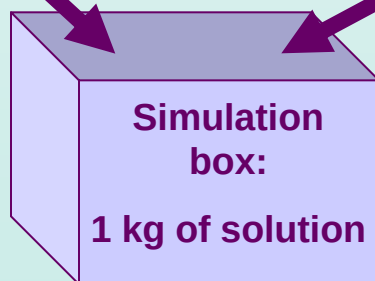


rock-fluid interactions



Fluid

Element	Molality
Na :	1.4 mmol.L ⁻¹
HCO ₃ ⁻ :	1.4 mmol.L ⁻¹
pH :	8.3
PO ₂ :	0.21 atm
pCO ₂ :	3.16 E ⁻⁰⁴ atm



Porosity : 20 %
Rock volume : 4000 cm³



Secondary minerals

Na-Beidellite

Zeolites :

Analcime
Chabazite Ca
Chabazite Na
Chlinoptilolite Na
Laumontite
Phillipsite Na
Phillipsite Ca

Chlorites :

Clinochlore
Daphnite

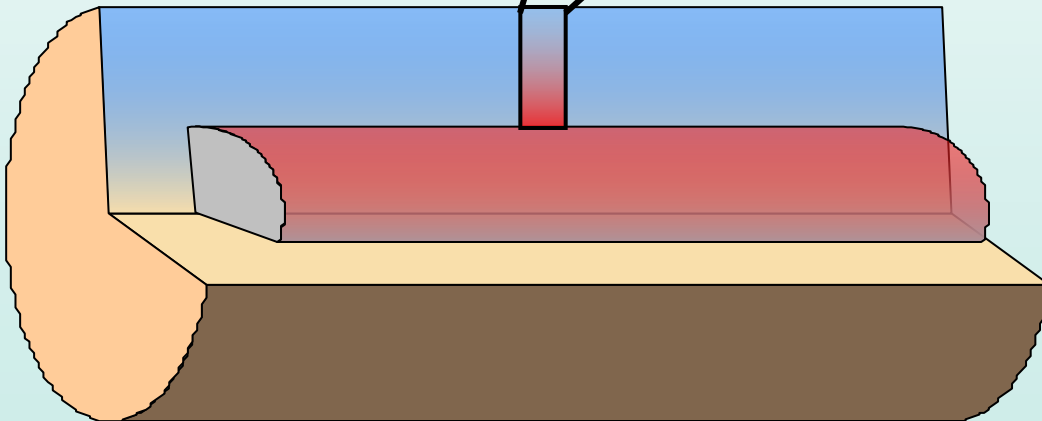
Saponites :

CaFe Saponite
CaMg Saponite
NaFe Saponite
NaMg Saponite

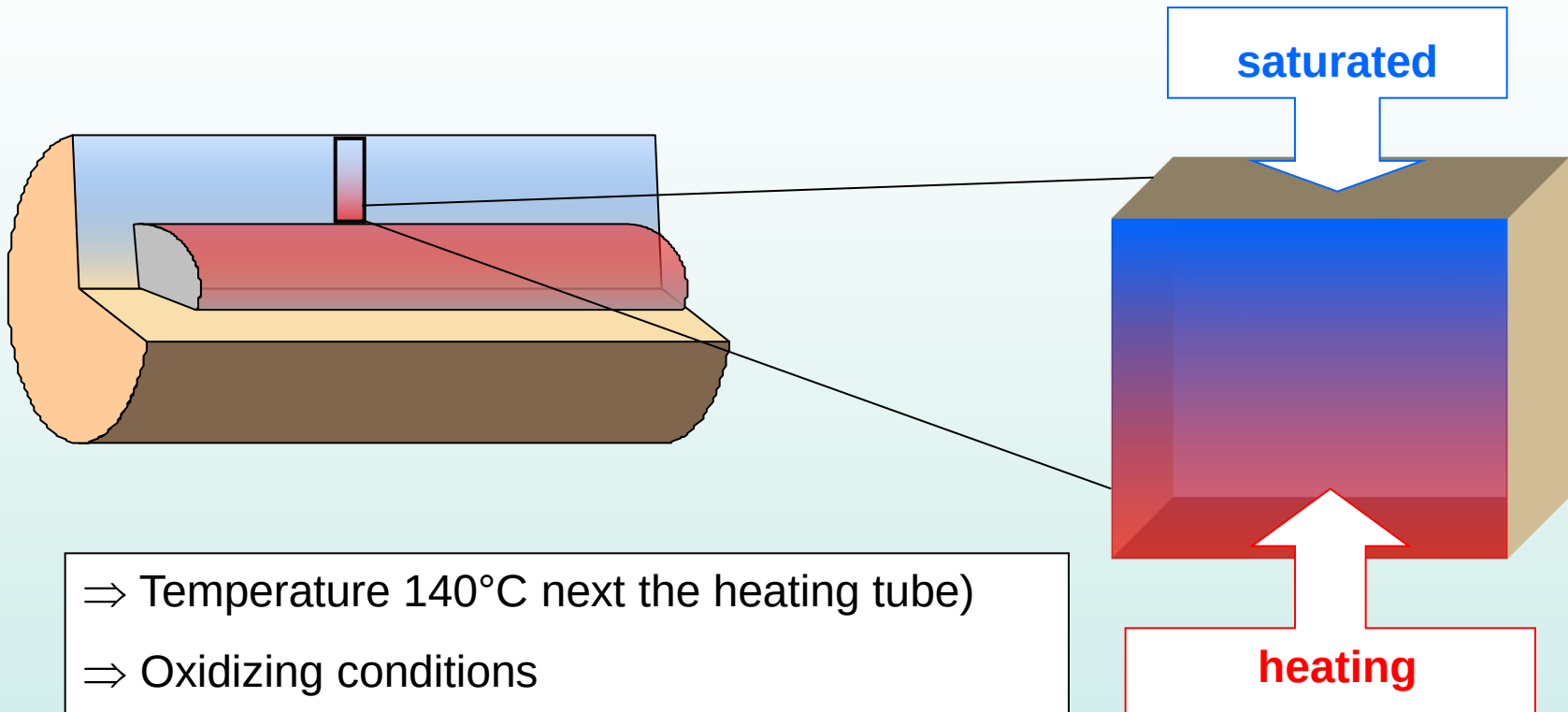
Others :

Amourphous Silica
Magnetite
Siderite
Anhydrite
Illite
Jarosite
Alunite

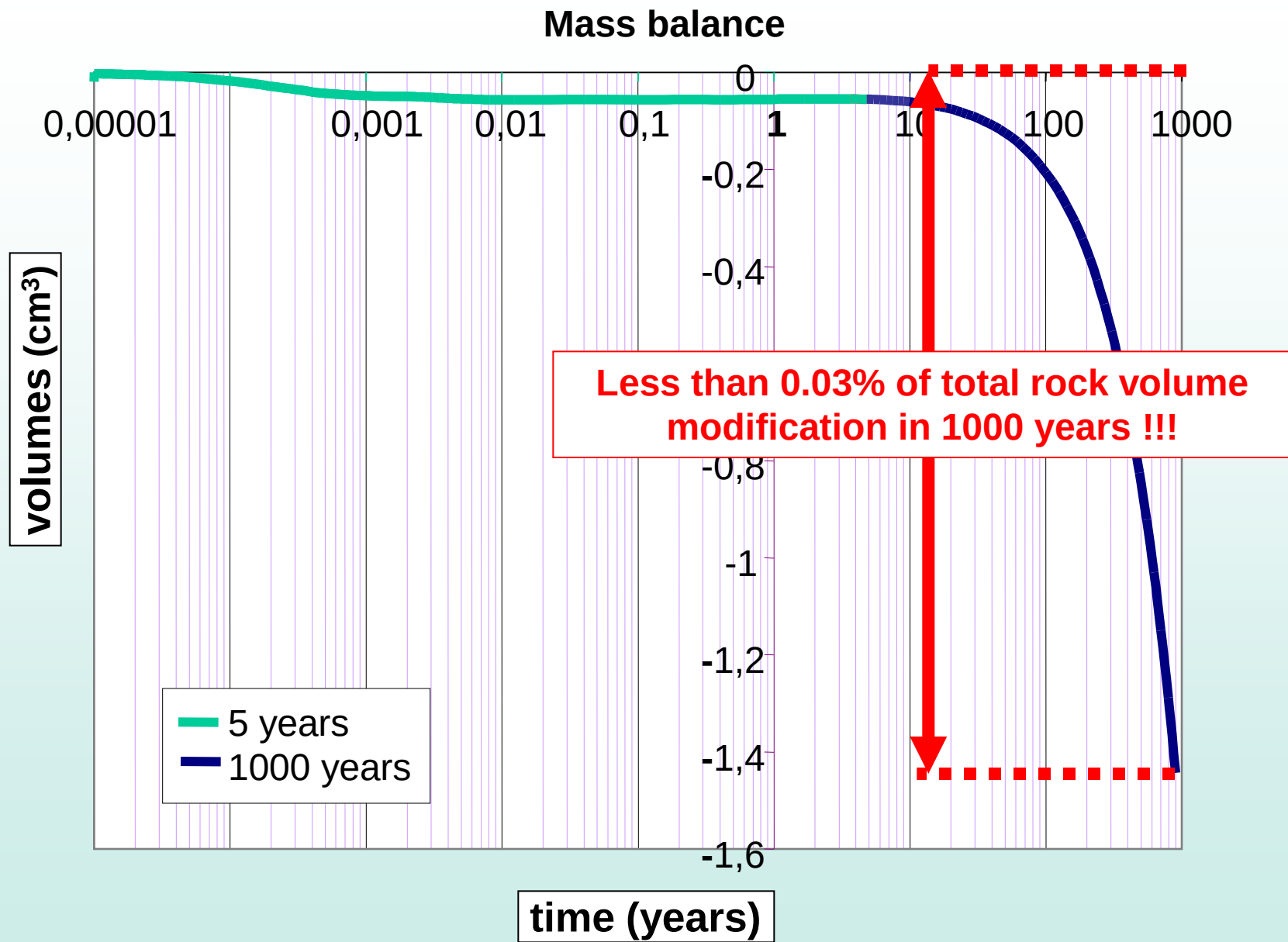
- Same conditions as samples (section 12,19)
- In the middle of the mock-up : to avoid edge effects
- near the central tube. The hottest points of the clay barrier are chemically the most reactive ones



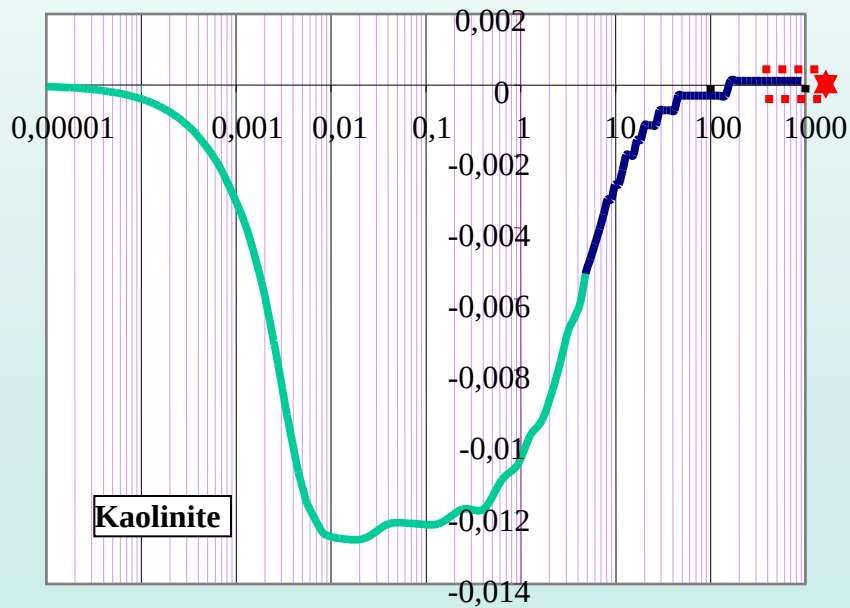
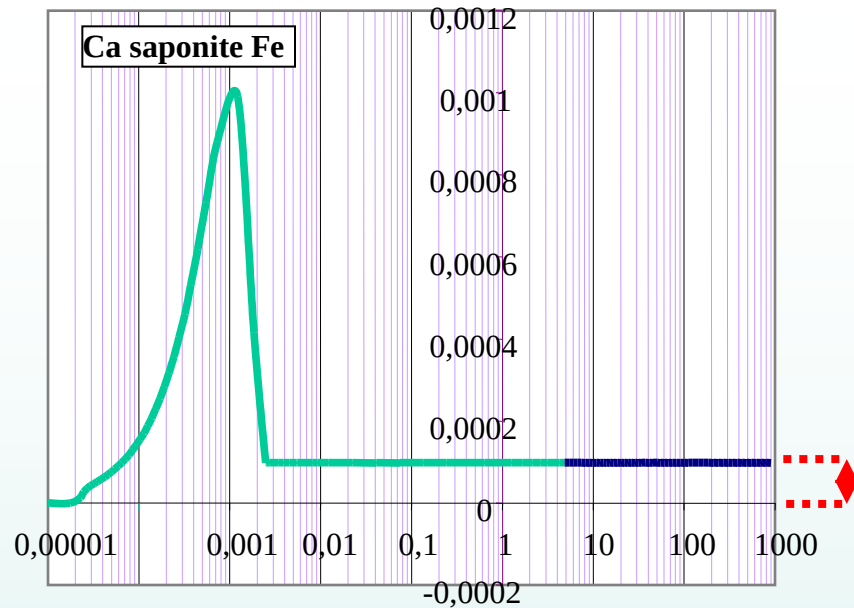
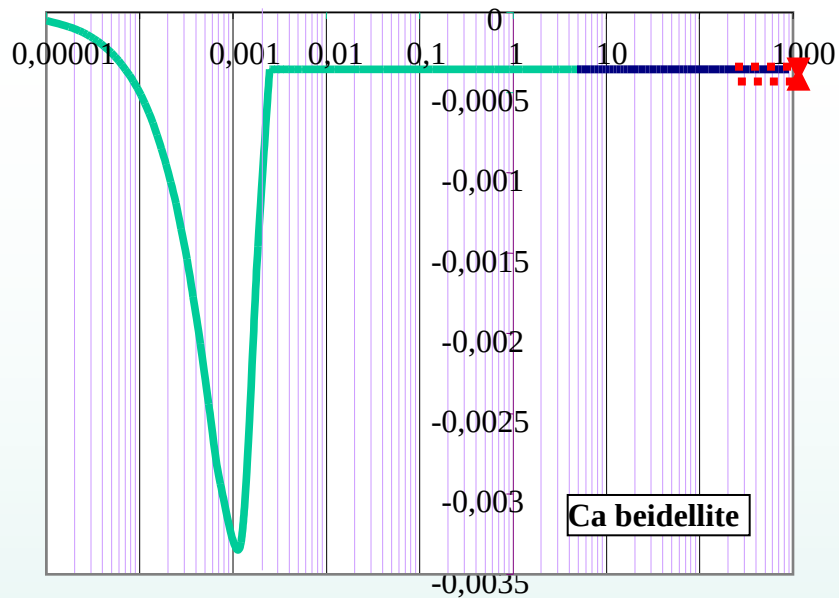
OPHELIE mock-up: batch simulation conditions



- ⇒ Temperature 140°C next the heating tube)
- ⇒ Oxidizing conditions
- ⇒ Closed system
- ⇒ Kinetics study 5 years-1000 years



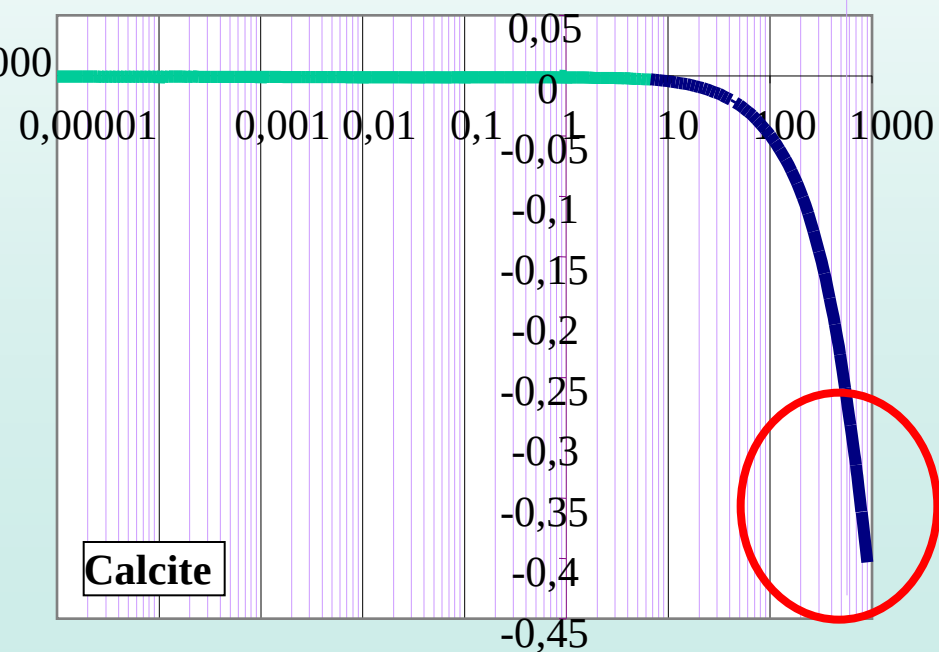
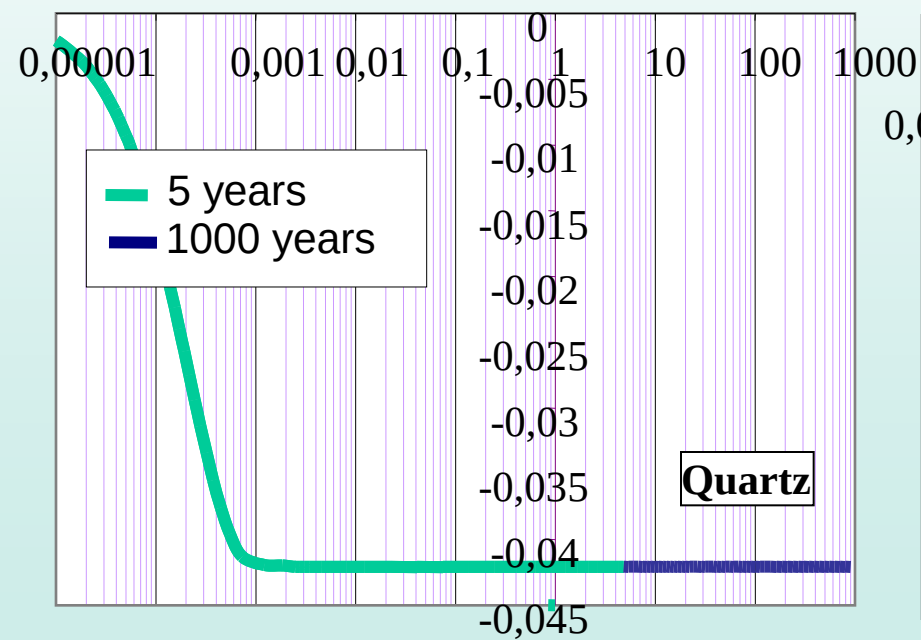
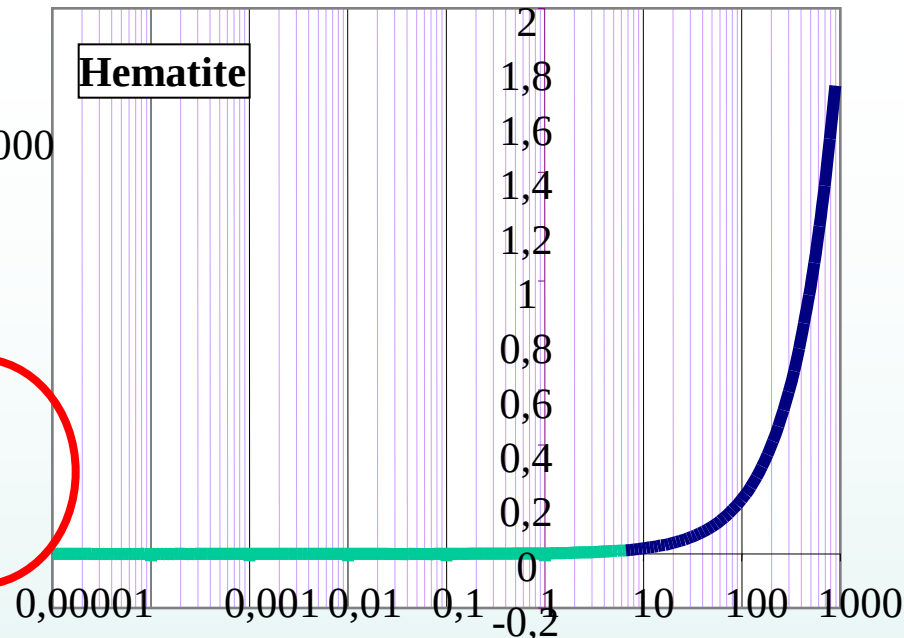
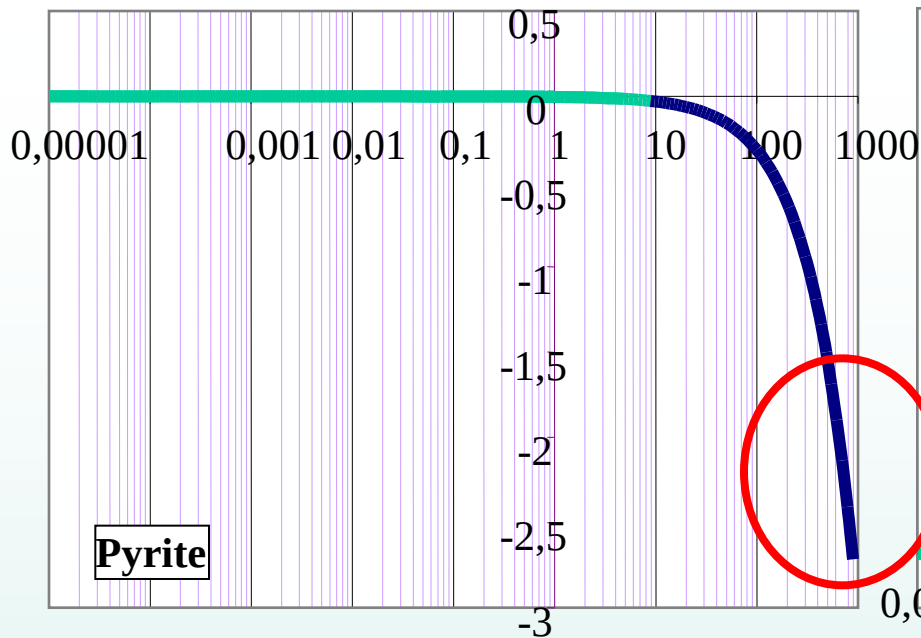
volumes (cm³)



time (years)

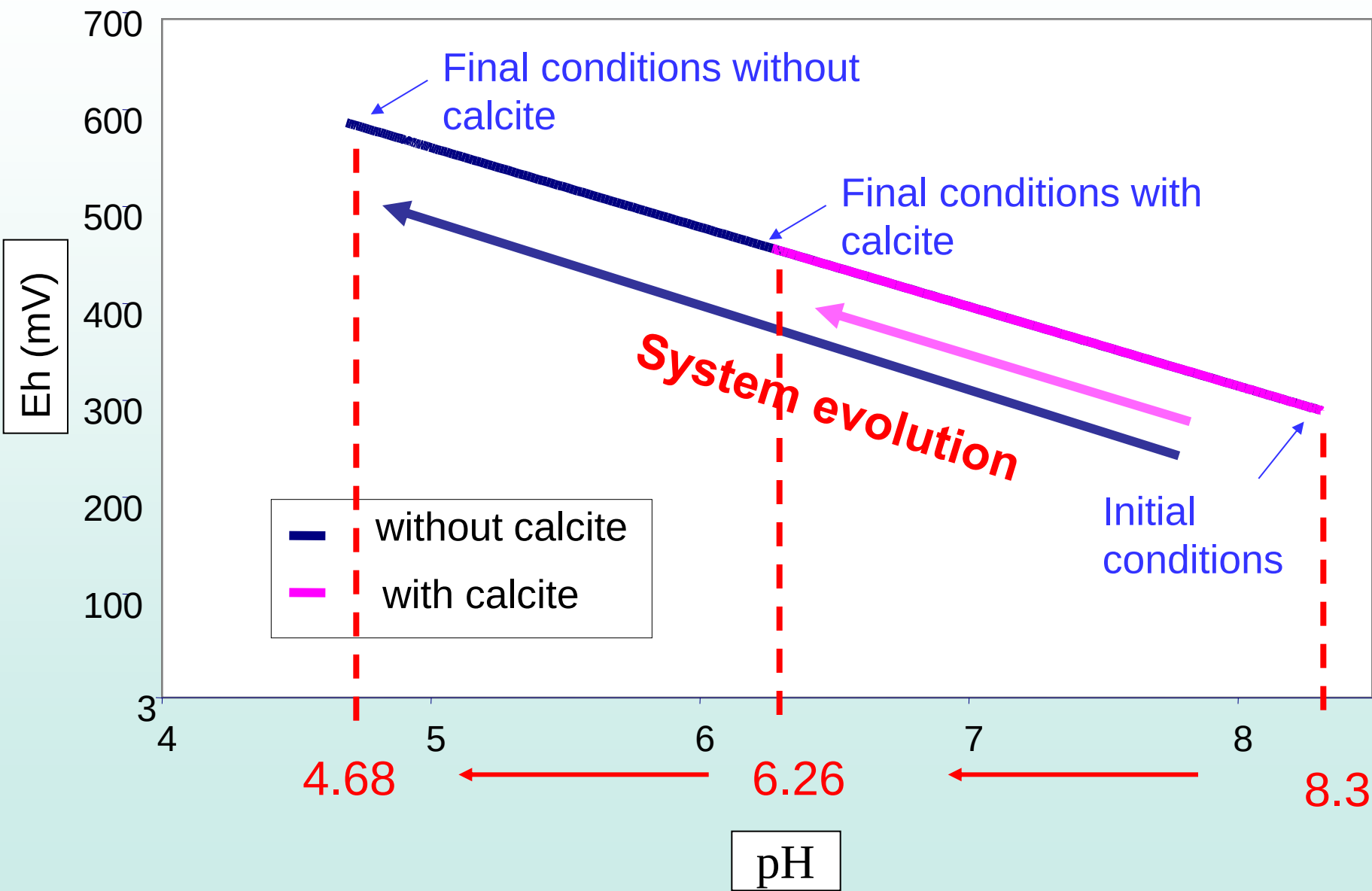
— 5 years
— 1000 years

volumes (cm³)



time (years)

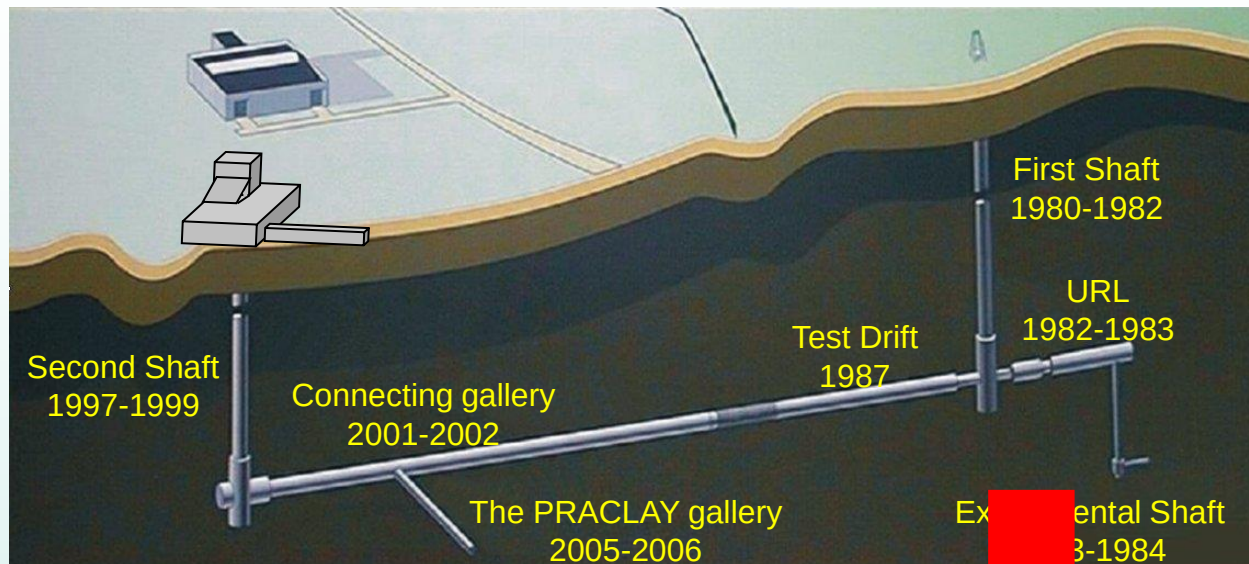
Pourbaix diagram



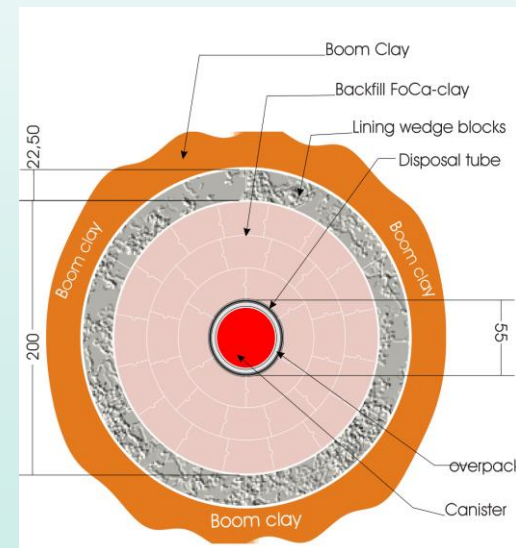


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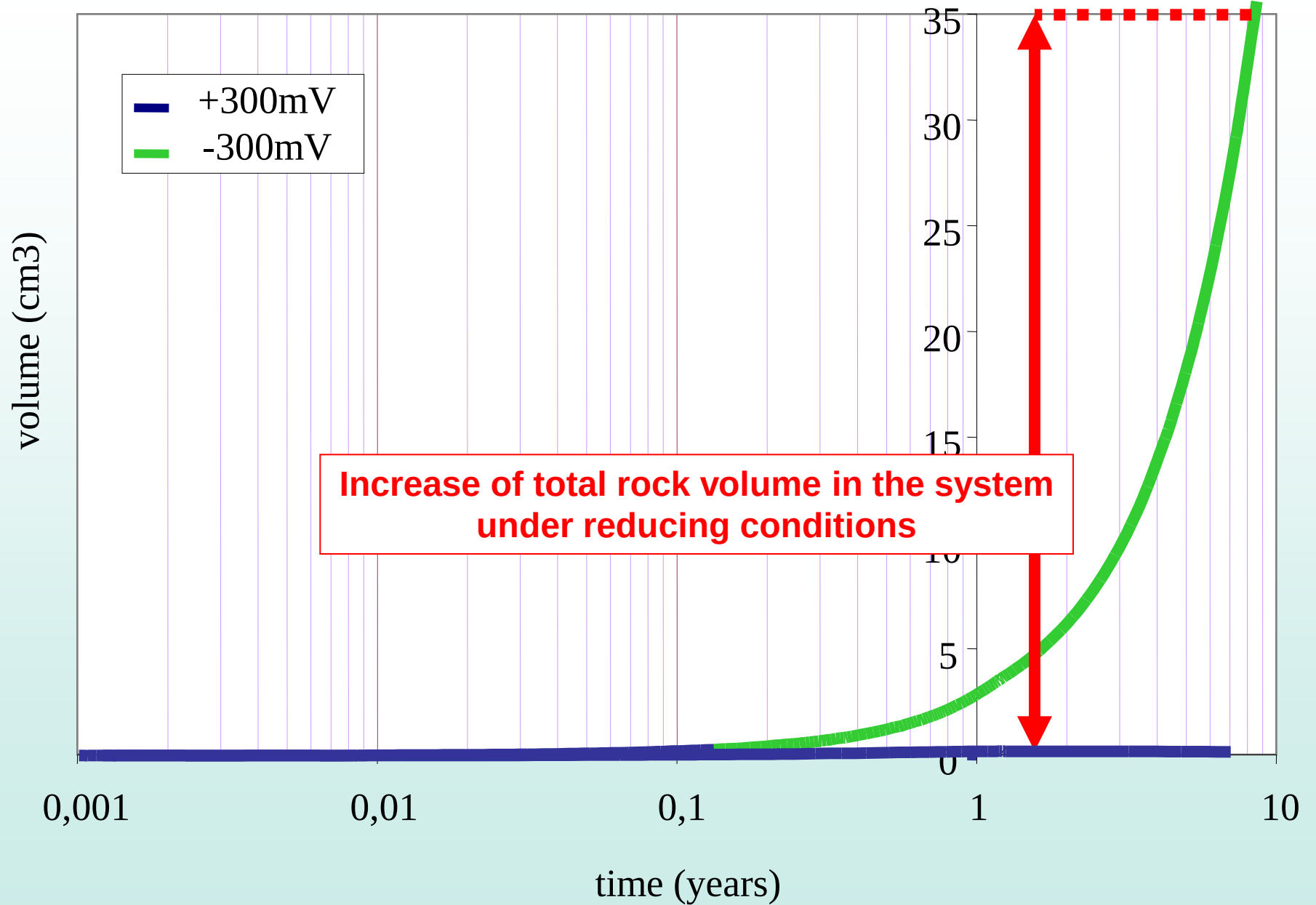
Sensitivity to the redox – underground conditions



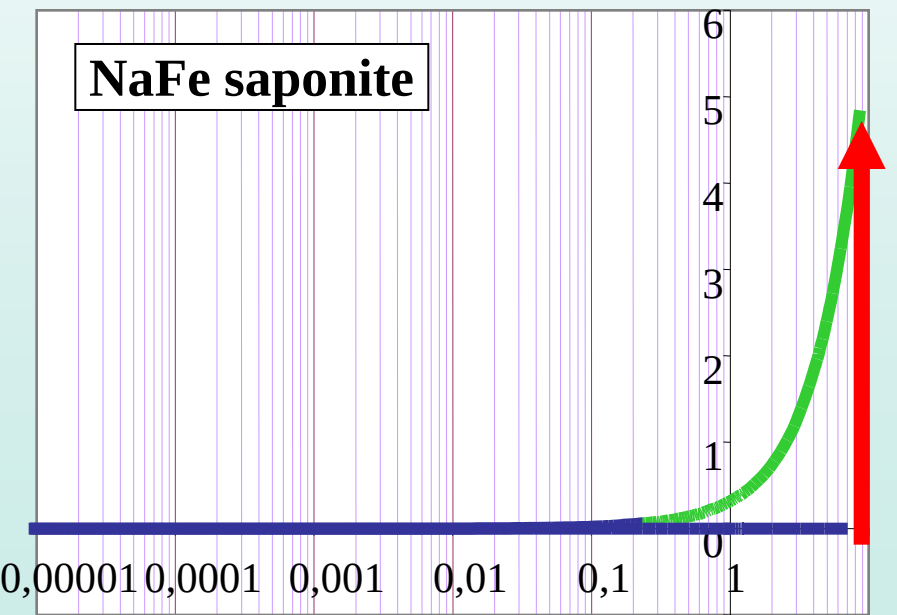
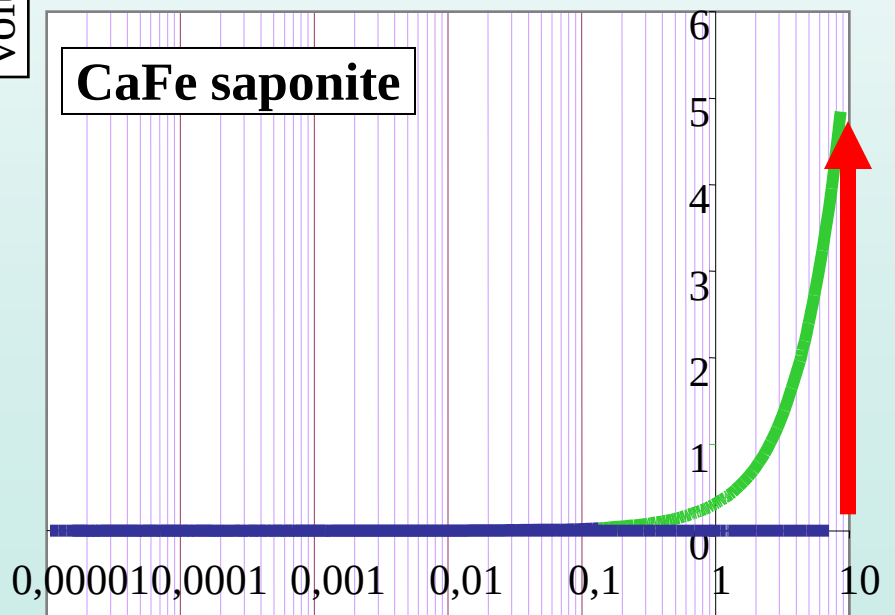
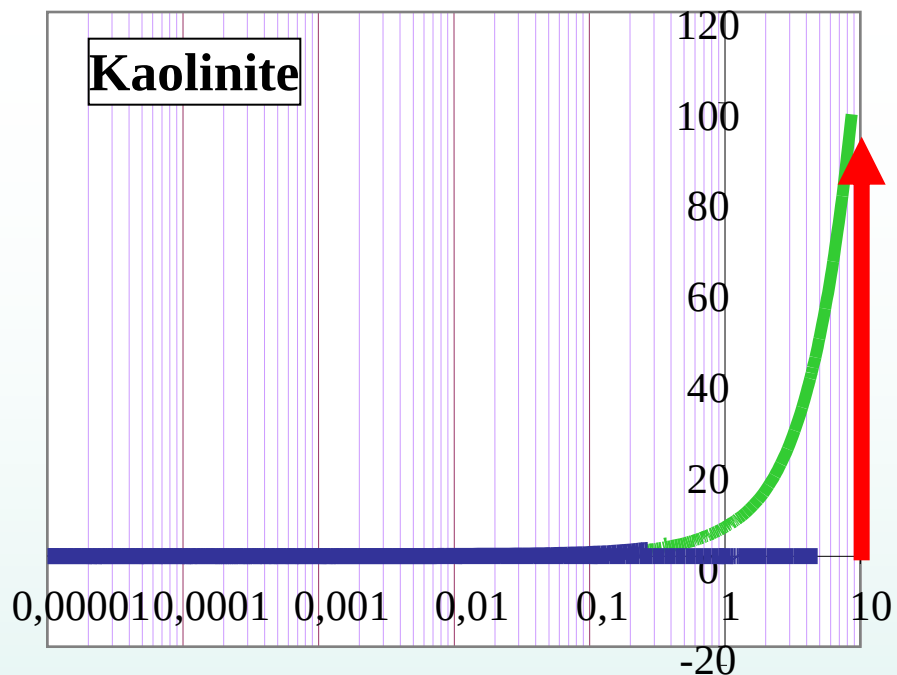
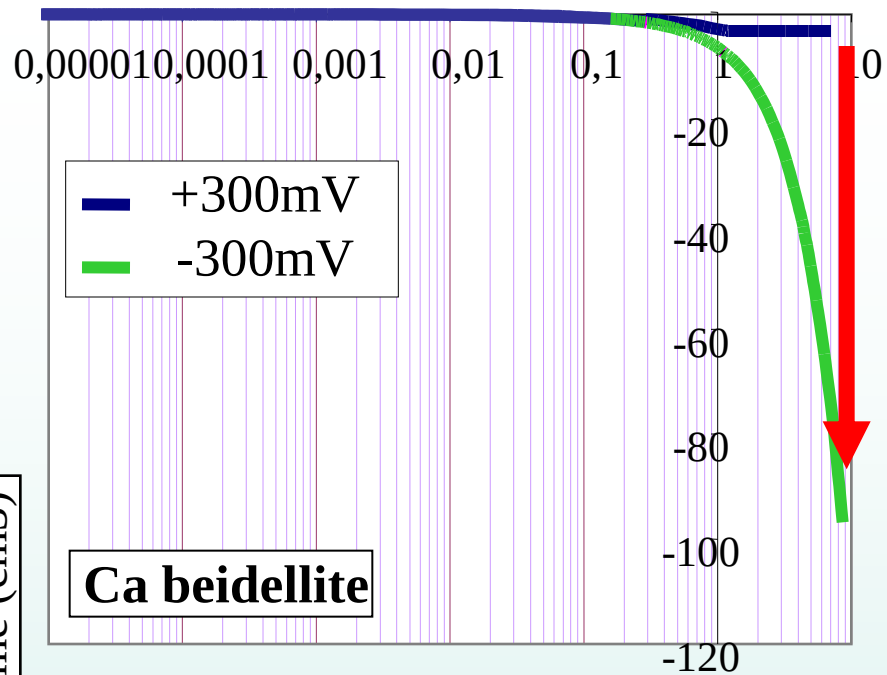
Underground conditions are reducing and not oxidizing anymore



Mass balance

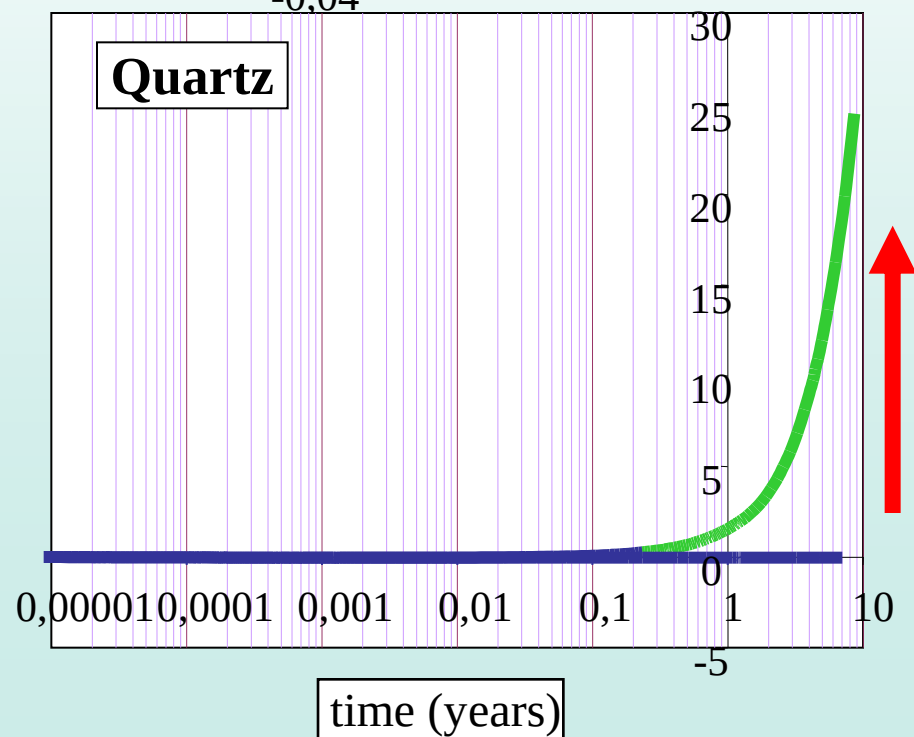
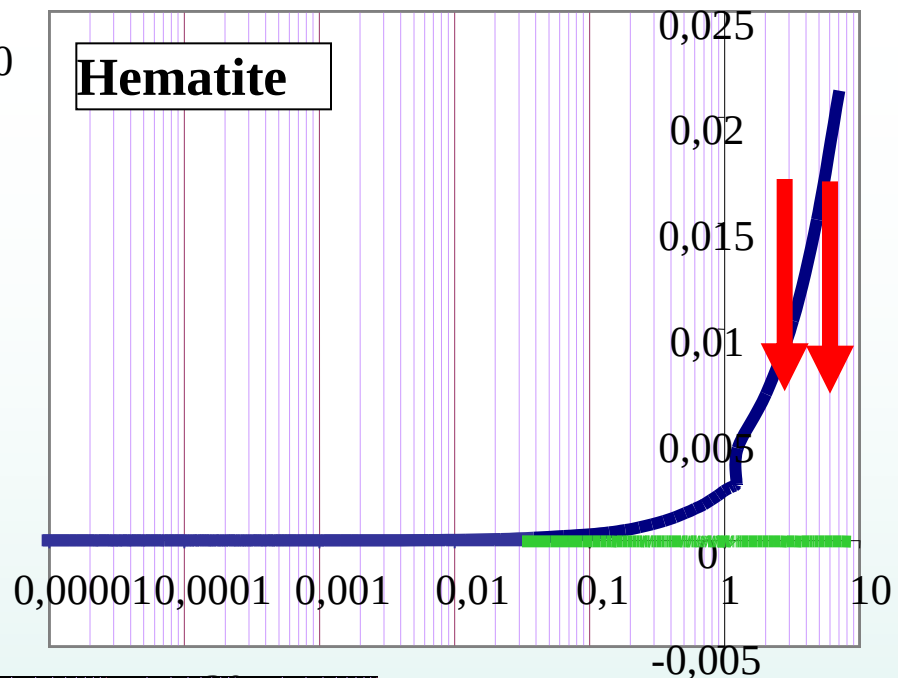
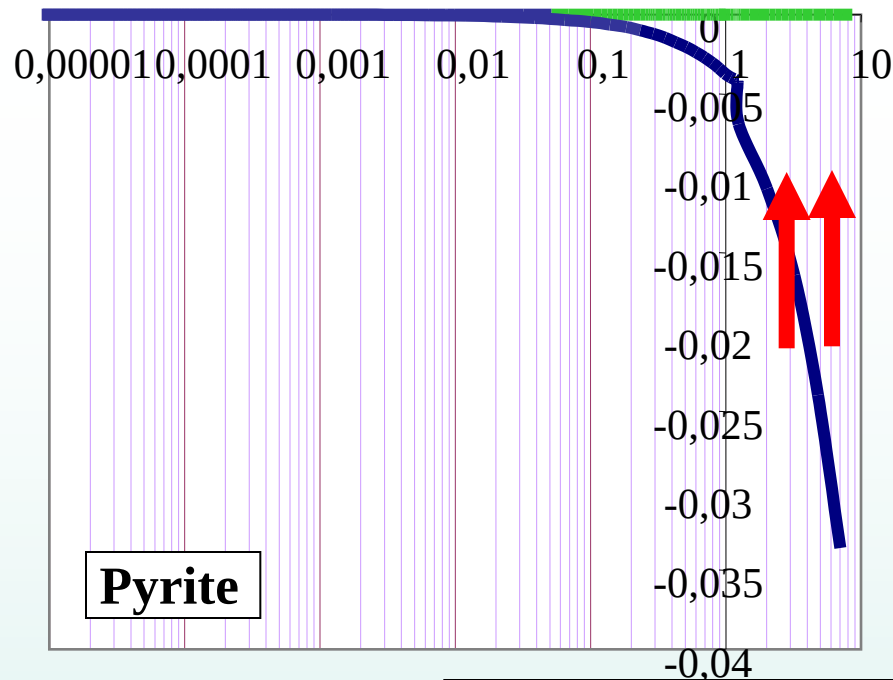


volume (cm³)



time (years)

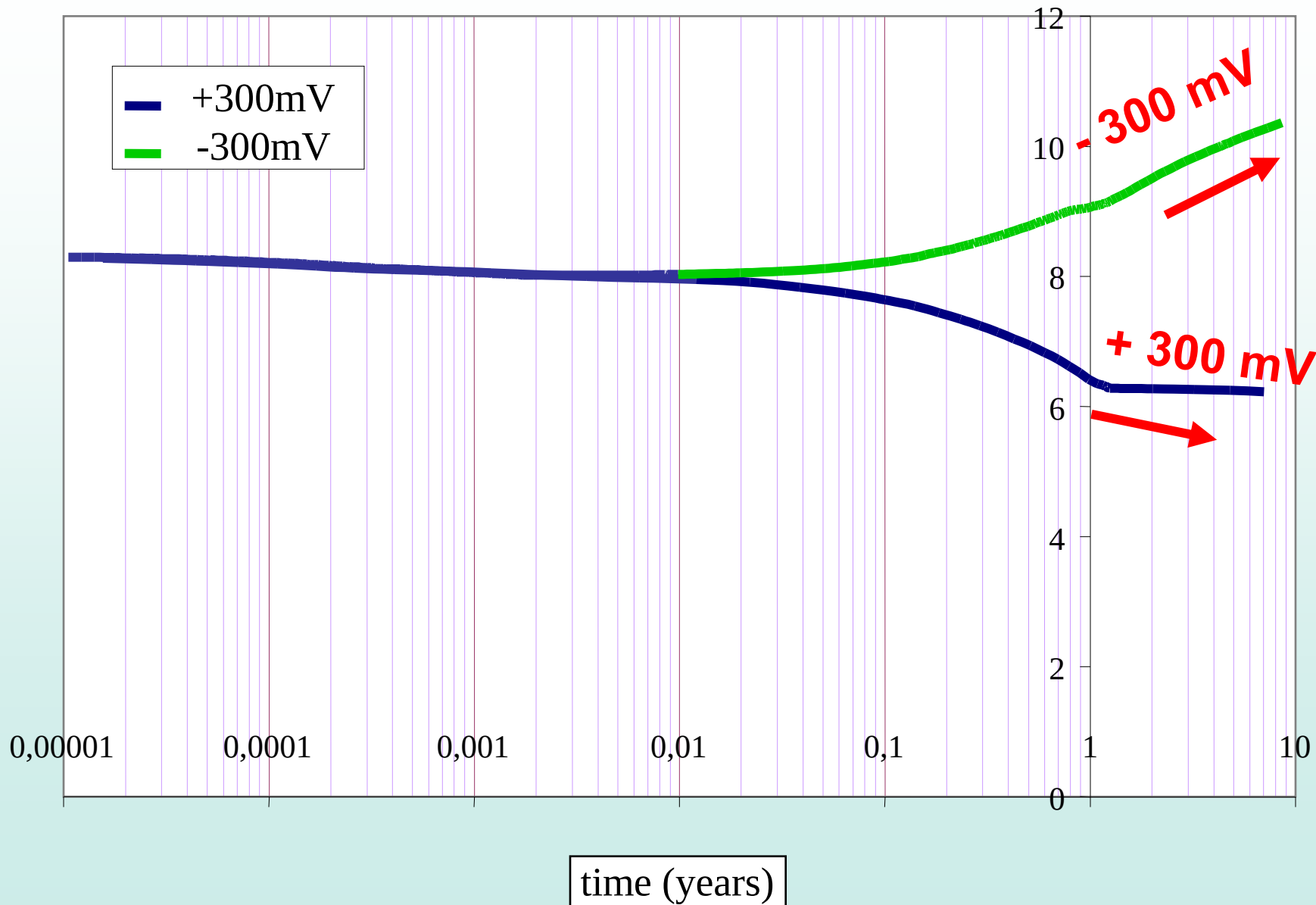
volume (cm³)



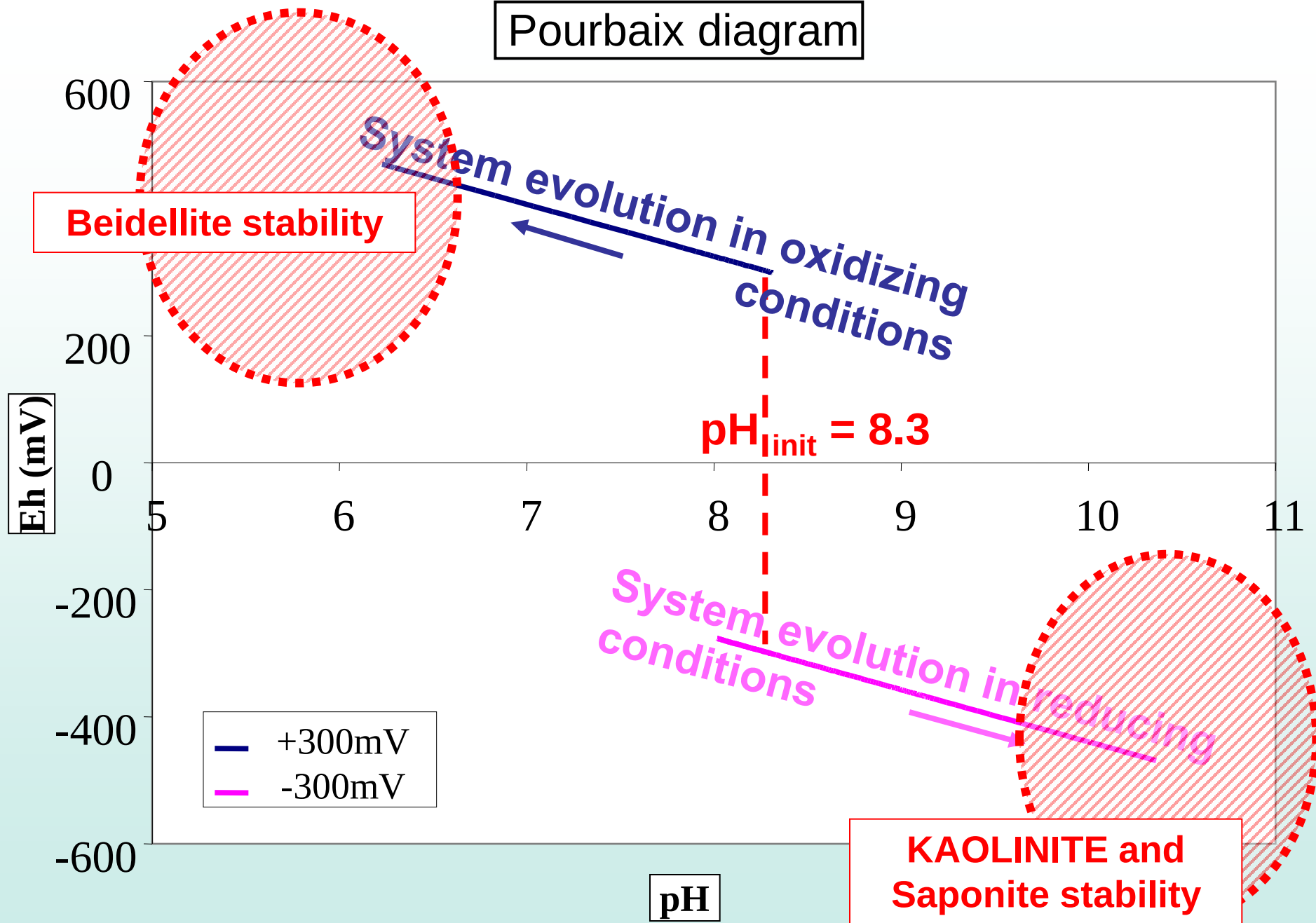
— +300mV
— -300mV

pH

pH



Pourbaix diagram





Conclusions

Modelling the geochemical behaviour of the mock-up OPHELIE, is a complementary study to analytical post-dismantling analysis.

- From the results of analytical post-dismantling analysis, modelling allows to understand which processes occur in the mock-up
 - ⇒ Extrapolation on the long term
 - ⇒ Highlight the role of accessory minerals such as calcite or pyrite
- Reach geochemical fields not studied during experiment changing some critical parameters of the system
 - ⇒ Testing reducing conditions
 - ⇒ Help to define a backfill material in term of chemical performance
 - ⇒ Studying the influence of geochemical interaction on some physical rock parameters such as porosity or swelling properties

The role of geochemistry and geochemical modelling in the Belgium Safety and Feasibility Case

Ann Dierckx

Euridice Exchange meeting – June 30th, 2004



Geochemistry and geochemical modelling in the Safety Case

- *The safety case is an integration of arguments and evidence that describe, quantify and substantiate the safety, and the level of confidence in the safety, of the geological disposal facility (NEA)*
- NIRAS/ONDRAF planning
 - 2013: Safety Case I (SFC I)
 - 2020: Safety Case II (SFC II)



Organisation of Safety Case

- Under construction....



Safety assessment (Models, codes, data + assessment)

Near Field

Geosphere

Biosphere

Source term
(waste)

Geochemical
datasets

Others



Geochemistry is one of the cornerstones of a sound assessment basis

- Sound assessment basis: the scientific and technical information and **understanding**, including the detailed support for the expected evolution of the disposal system and assessments of the uncertainties in scientific understanding (*NEA, Safety Case*)



Understanding: to what level of detail?

- *“In particular, a balance should be struck between building a predictive capability based on realism and mechanistic understanding and a capability to support safety through robust models and arguments” (NEA, IRT)*



Different levels of understanding – Model concepts

- Proces understanding at nm scale > ... > Formation scale models (PA)
 - Research models > Qualitative understanding of mechanisms > Lumped processes and heterogeneity in a single parameter
 - *E.g.* surface complexation > solubility enhancing factor caused by organic matter > K_d
 - Soft data – qualitative arguments (natural evidence)



Level of understanding in relation to the safety functions of the different components

- Host rock – *Diffusion and retention (R2)*
 - *“For modelling the solubility and the retention of radionuclides, a more detailed understanding of the interactions between water and minerals is recommended. Moreover, the IRT notes that a mechanistic sorption model specific to the Boom Clay (for major elements and the significant radionuclides) is missing.” (IRT, NEA)*
 - Ultimate barrier
 - Robust approach
 - Past: Migration experiments
 - Foreseen: Batch experiments – test “mechanistic” modelling – macroscopic scale – aim: process based geochemical database?



Understanding – Host rock perturbations

- Foreseen: Perturbations induced by construction and operation of repository
 - Measure the impact of heat, oxidation, use of concrete (buffer and construction) on the “geochemistry”
 - Assess the extent of the impact
 - Degree of detail?
 - Depends on the previous and next point
 - Assess the consequence of the perturbation on the function of the host rock – *diffusion and retention*
 - Degree of detail?
- Degree of detail will be balanced with respect towards the extent of the perturbation and its consequence on the safety function



Understanding – Engineered Barrier System (EBS)

- “*More attention should be paid to the geochemical evolution of the EBS.*” (IRT, NEA)
- Level of understanding is again in relation with the safety function attributed to the different components and with the relative importance of the safety function attributed to all components
- Needs are under discussion
- Present activity: Scoping calculation of the geochemical environment in relation to safety function *water tightness* (C1) of overpack
- Scoping will be tested against available R&D results (CEA,)



Understanding – Engineered Barrier System

- First step: Define approach to arrive to a common geochemical environment for experiments and modelling.
- Next steps: Collect data to assess the retention



Understanding – Waste Packages

- Geochemical modelling is used to assist in the overall understanding of dissolution behaviour



Safety assessment (Models, codes, data + assessment)

Near Field

Geosphere

Biosphere

Source term
(waste)

Geochemical
datasets

Others



Model concepts used in PA

- To assess the retention
 - Solubility
 - Sorption: K_D model is used
 - Other model concepts could be discussed
- R&D challenge: Are research models needed?
 - EC 6th framework: Funmig



Hard data for PA

- TDB: Thermodynamic database
 - NEA review, PSI, H12, ...
- GDB: Geochemical database
 - Introduction of process understanding (mechanistic modelling) for a given host-rock, under predefined environmental conditions (pH, E_H)
- DCFs: Data collection forms (sorption and solubility values)
 - Conditional experimental data (in house + literature data under comparable conditions)
 - Geochemical modelling (input from TDB and (?) GDB)



Quality policy: formal organisation

- The databases in the Belgian programme
 - Boom Clay description – common equilibrium model for the porewater
 - Thermodynamic Databases (TDBs)
 - Sorption and Solubility Databases (DCFs)
 - Geochemical Databases (GDBs)
 - Near field description – common porewater composition (can be different $f(\text{time, application})$)
- The codes used
- The use of the codes



Practical implementation (1)

- Group of modellers organised around one central coordinator (role for this task force?)
- Tasks for the task force and coordinator
 - Central database keeper: keep record of all decisions
 - Central version keeper: keep “online” record of the versions of the models and codes
 - Screening of current models in use in view of their application area, their advantages, disadvantages, ...
 - What models do we keep in our basket?
 - Representation of the geochemical aspects of the Belgian Programme internally - externally



Practical implementation (2)

- Organisation of reflection moment whenever an activity or group of activities that touches the field of geochemistry, both modelling and experiments, is considered. And this over the complete Belgian Programme: Waste Packages, Geological Disposal, Euridice, Third Parties, ...



Conclusion

- Geochemistry is considered as one of the cornerstones in the assessment basis of SFC
- Degree of detail is dependent on the safety functions of the different system components and their relative weight
- Formal organisation of geochemical activities

