

# **Modeling on uranium geochemistry and spent fuel**

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**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

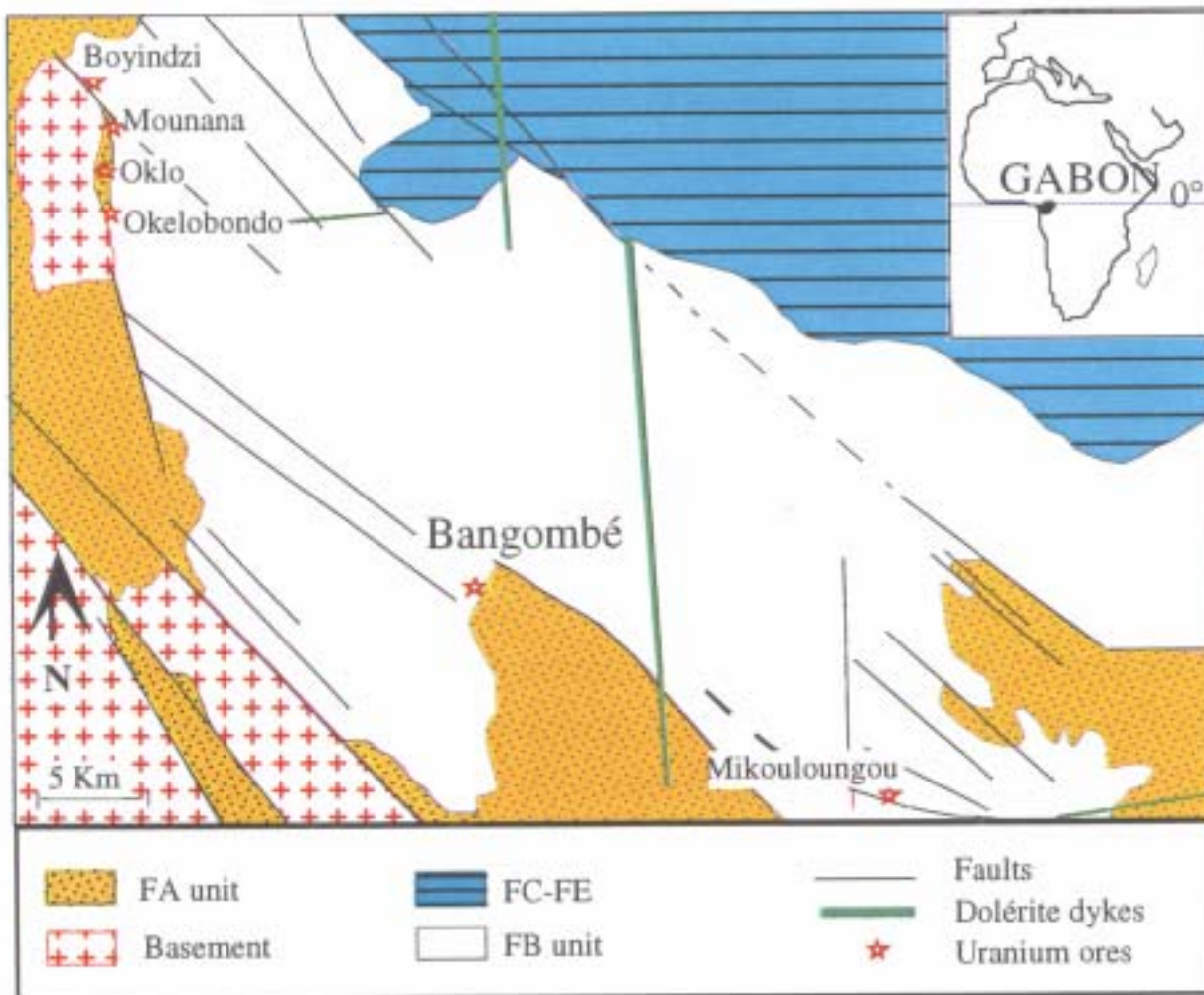


Uranium mineralization

**1950 My**



# Location of uranium ore deposits



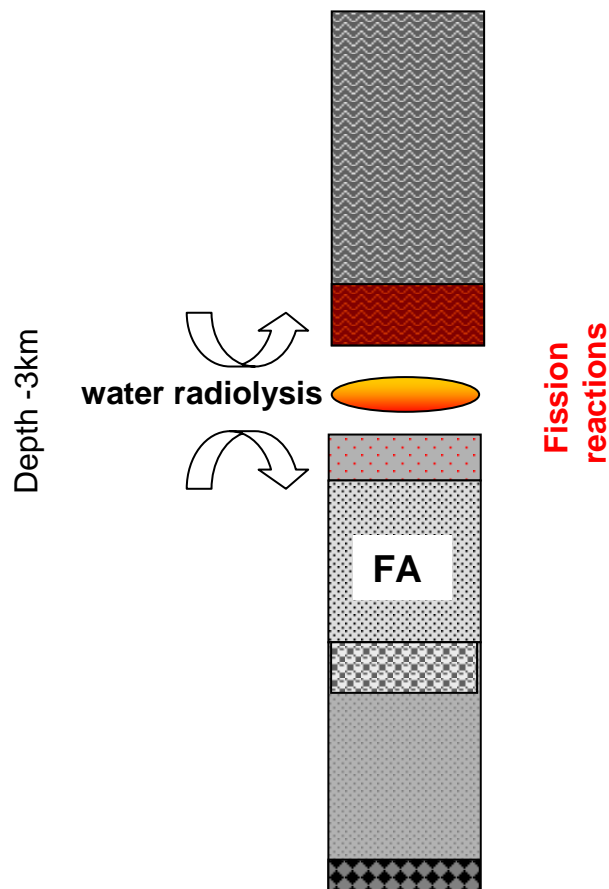
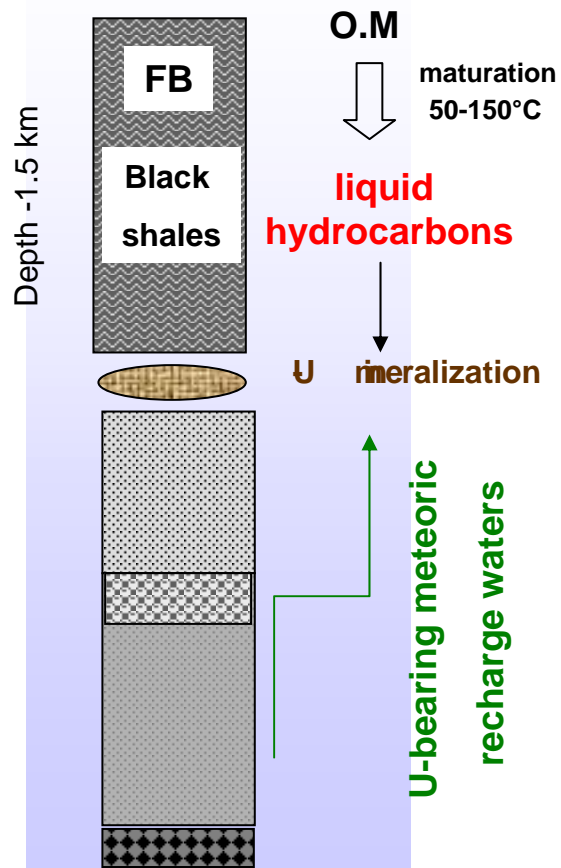
# History

**2050 My** Ore-stage

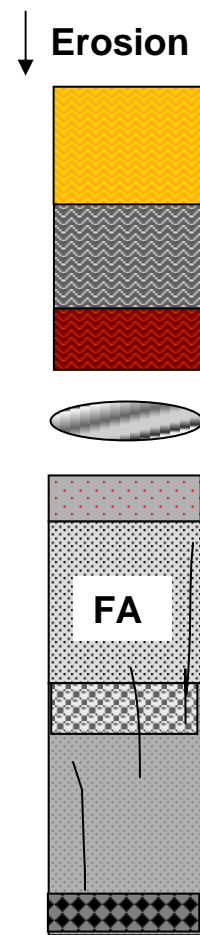
**1970 My** Reactive stage

**350 Ky** Post-ore stage

Diagenetic and hydraulic fracturing



Onset of supergene weathering



unfolding

# Problem of radioactive waste disposal



## Definition (Côme and Chapman, 1986)

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

# MATERIALS

## Uraninites of reactor core

Spent fuel produced in artificial power plants



**UO<sub>2</sub>-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**

# PROCESSES

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Elapsed time



**Long-term behaviour of radionuclides**

**= Release, transport and retardation processes**

Effects of water radiolysis (=decomposition of water)

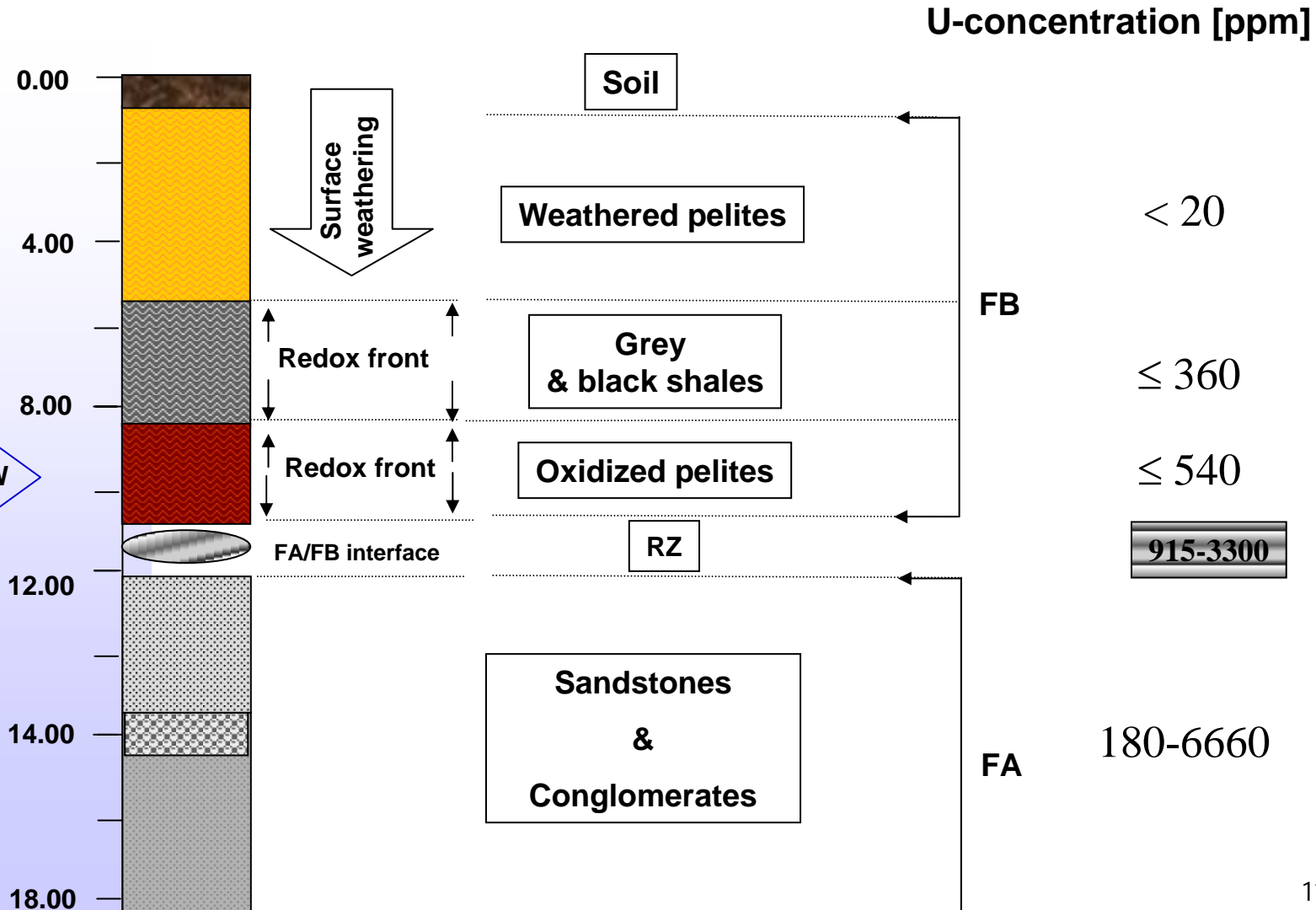


**e.g. oxidation phenomena**

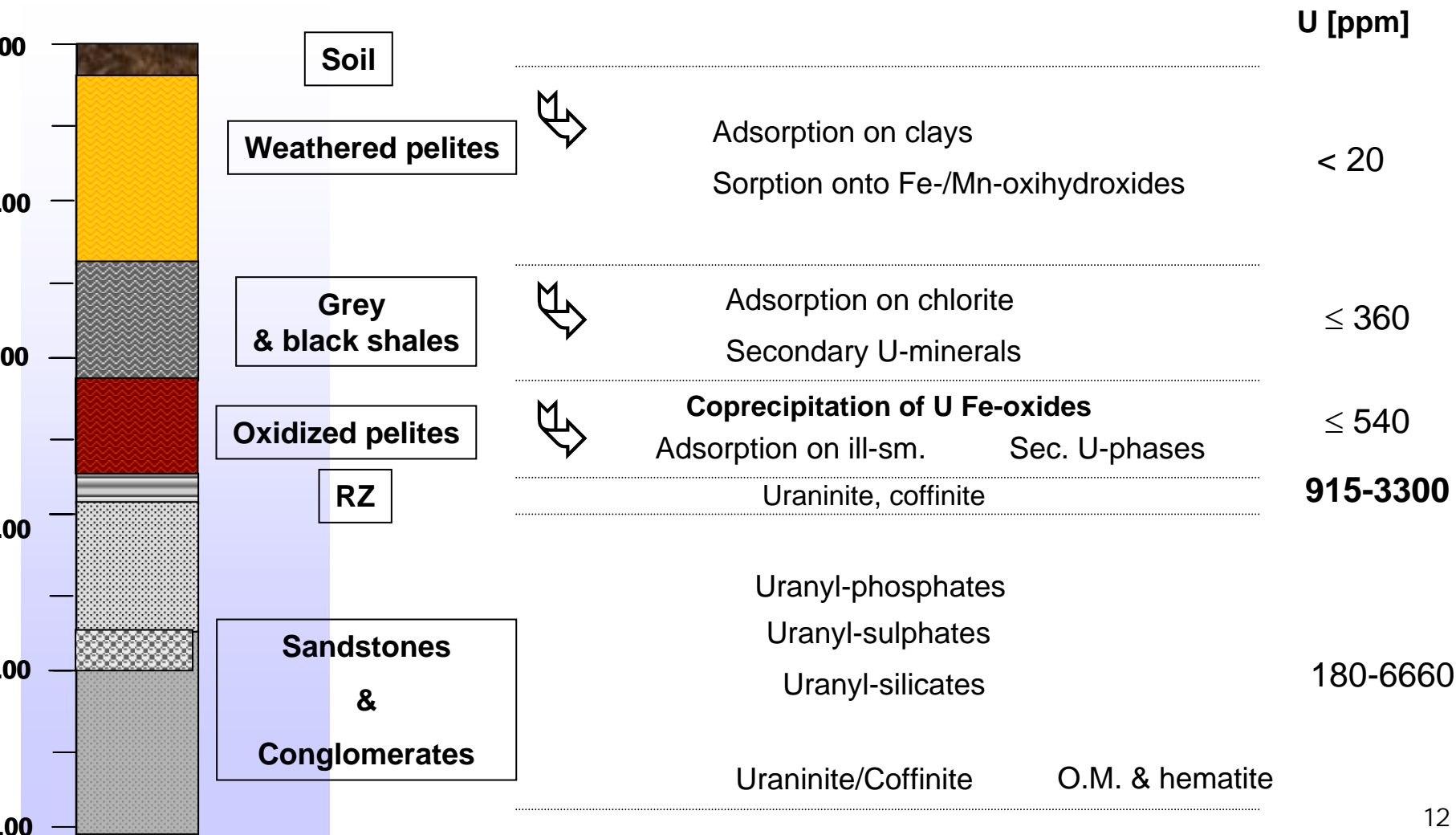
# Modeling example

Present day U-migration/retention processes

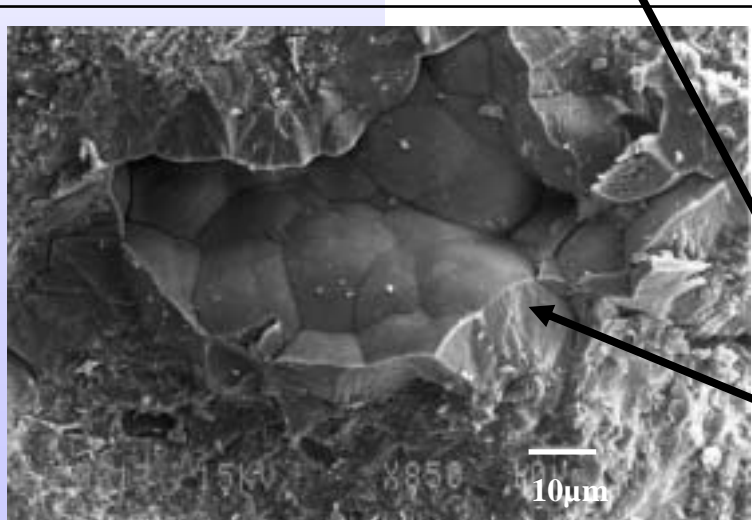
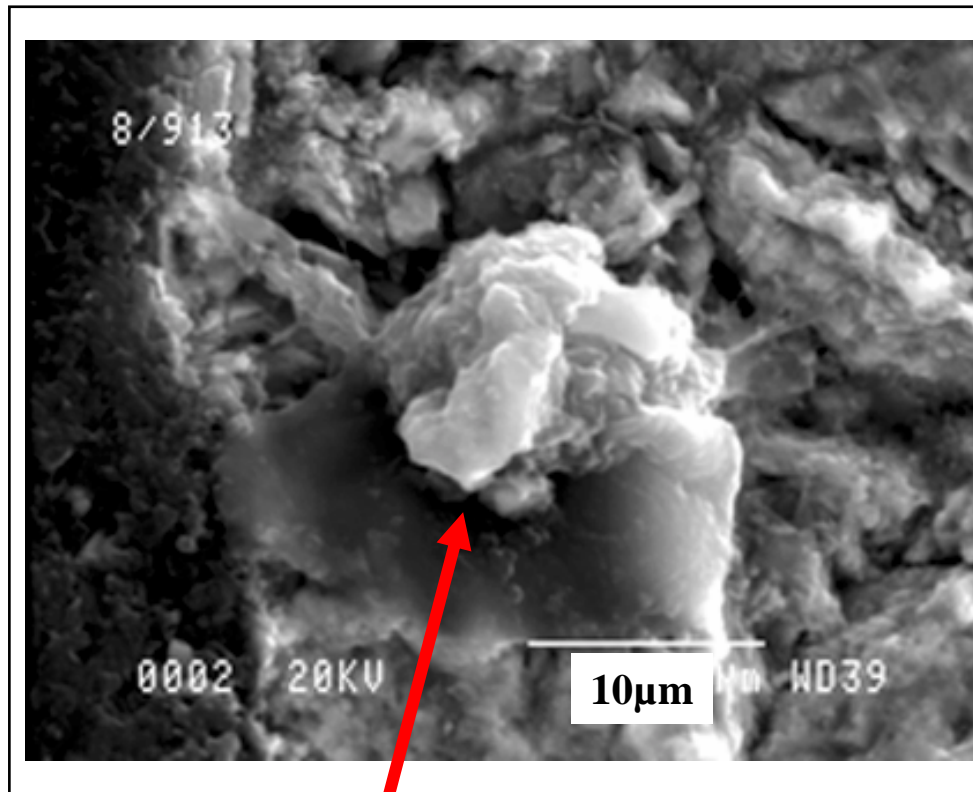
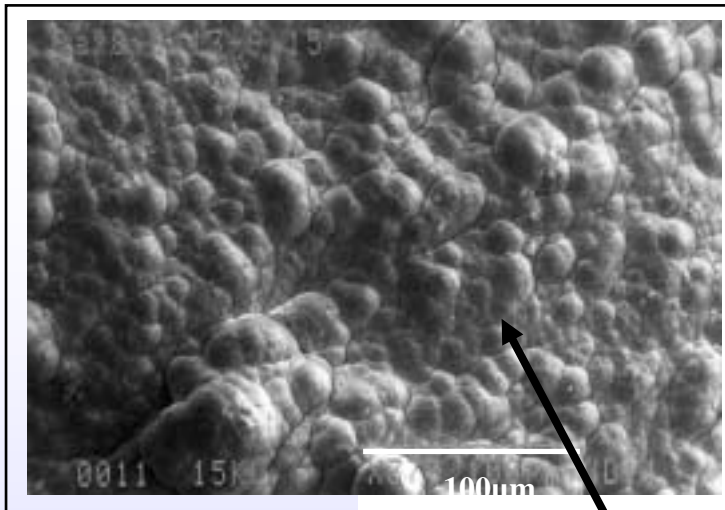
# U-distribution in the rocks



# U-retention mechanisms



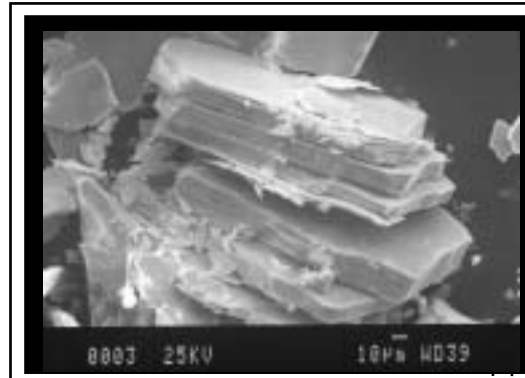
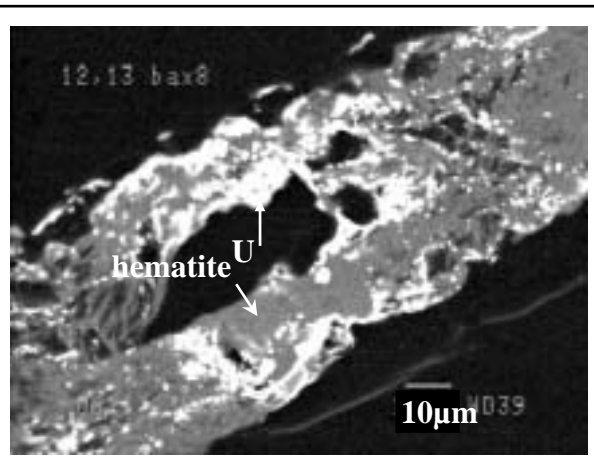
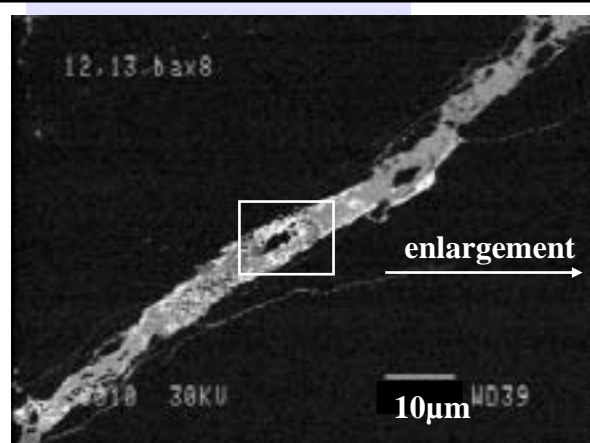
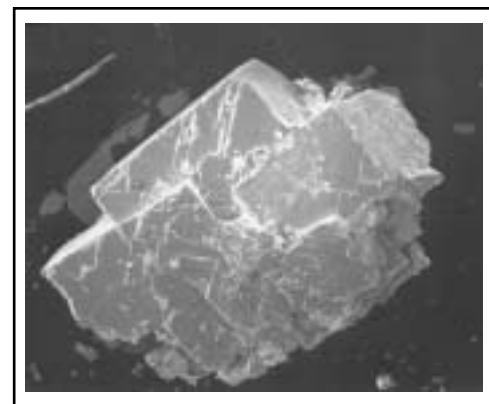
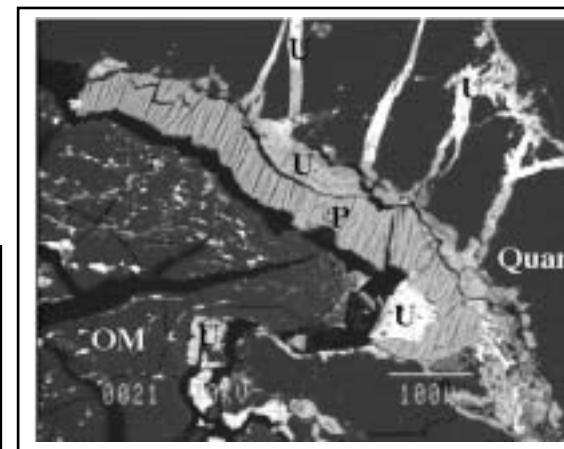
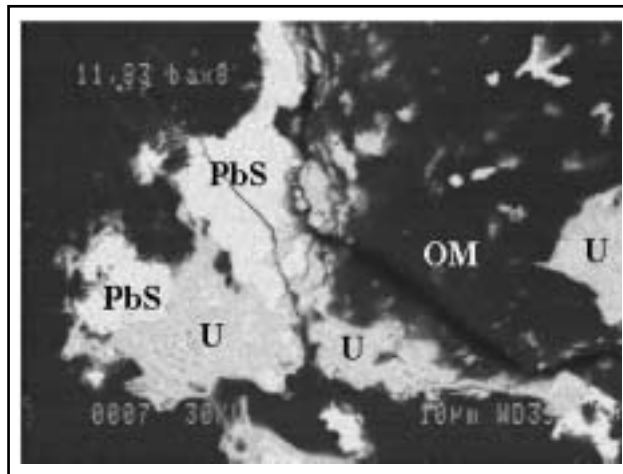
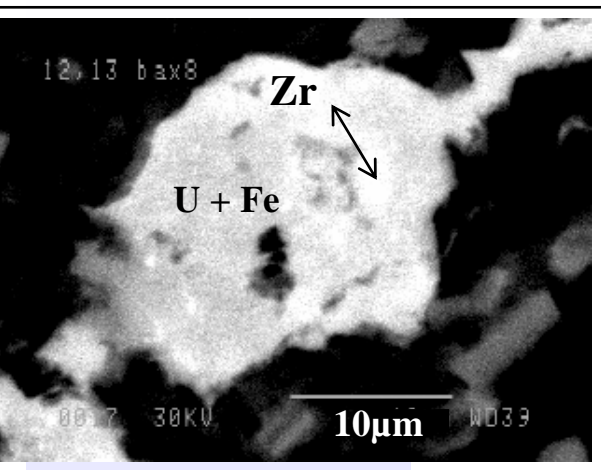
# SEM images of oxidized pelites FA/FB interface



**“autunite - like” overgrowth**

**Spherical goethite aggregates**

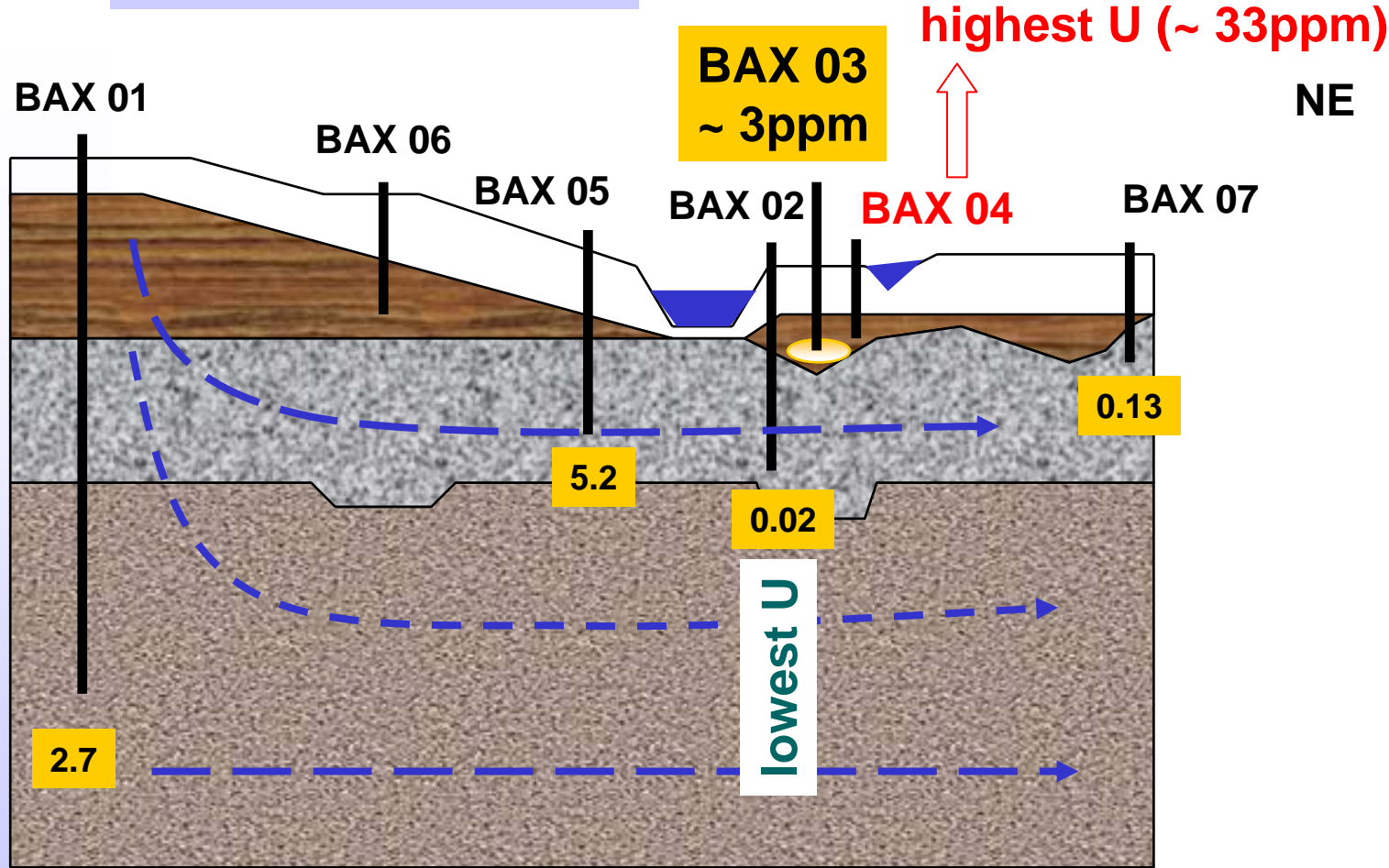
# FA formation



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

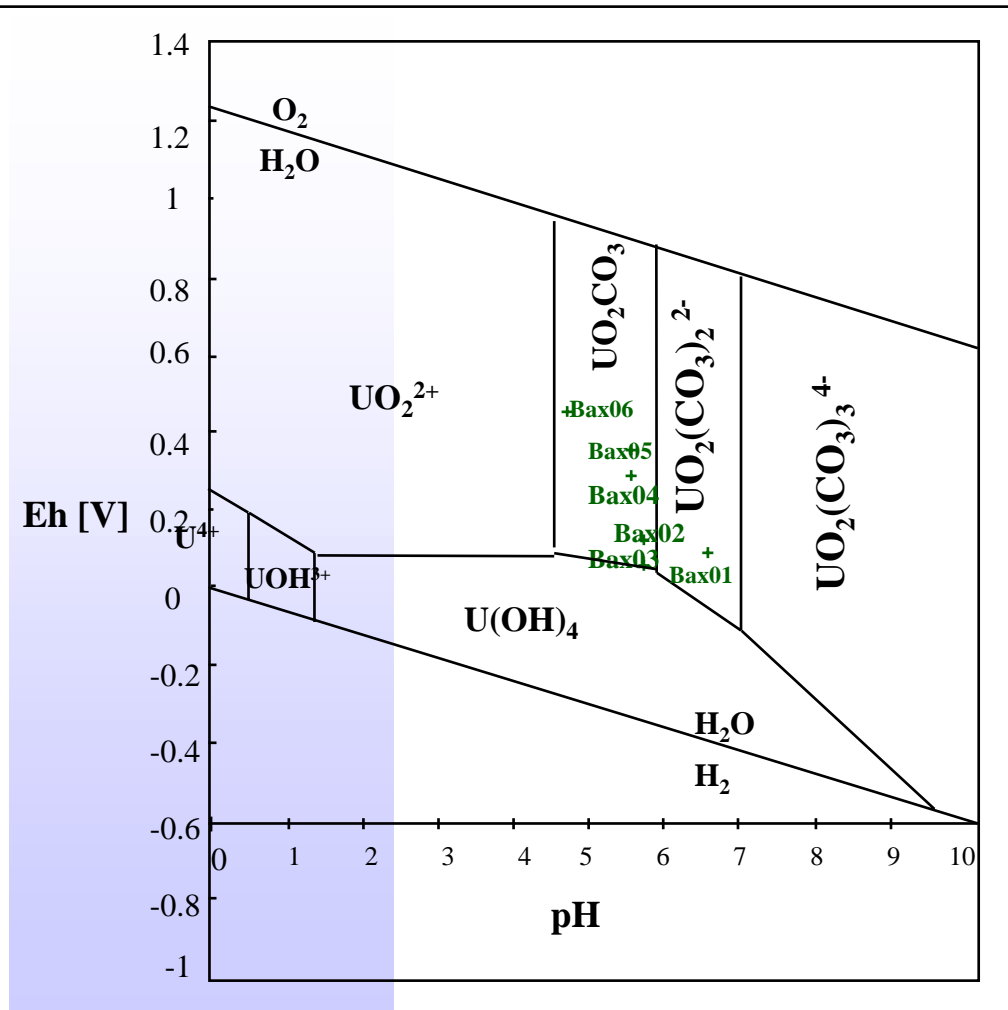
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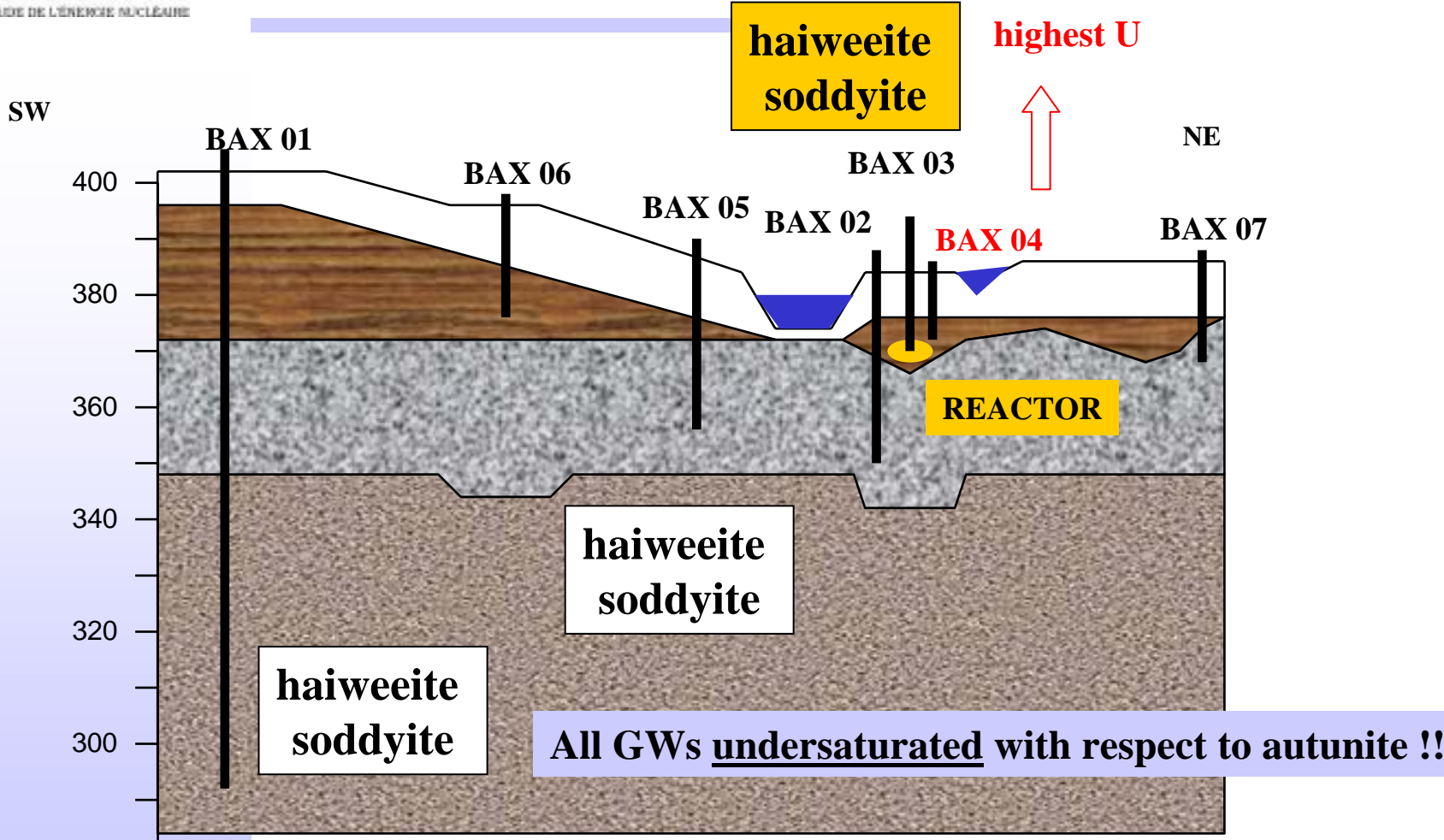
Scale  
 15m

- Alterites
- Pelites (FB formation)
- Sandstones (FA formation «unit a»)
- Sandstones (FA formation «unit b»)



**Dominant aq. U-species**  
 ↓  
**Uranyl-carbonate-complexes**  
  
**UO<sub>2</sub>CO<sub>3</sub>**  
 and  
**UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>**

# Calculation of saturation indices for U-minerals



Scale  
15m

- Alterites
- Pelites (FB formation)
- Sandstones (FA formation «unit a»)
- Sandstones (FA formation «unit b»)

## 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  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  redox pair  
dissolution of siderite and precipitation of amorphous iron oxide  
governing  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio**

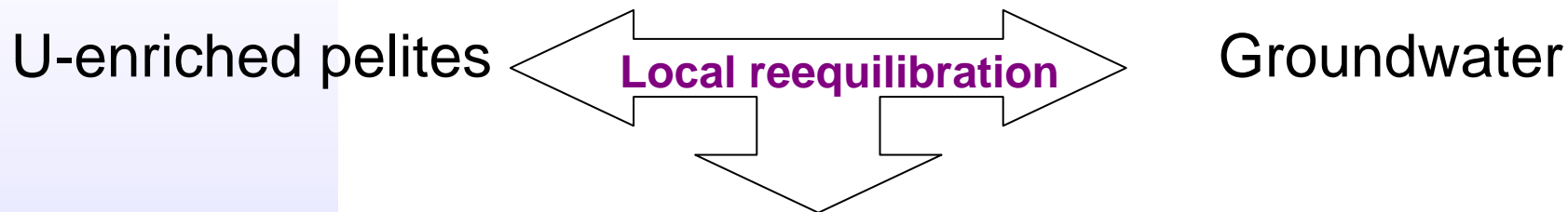
# Question

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

# Assumption

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**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  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{SiO}_2$

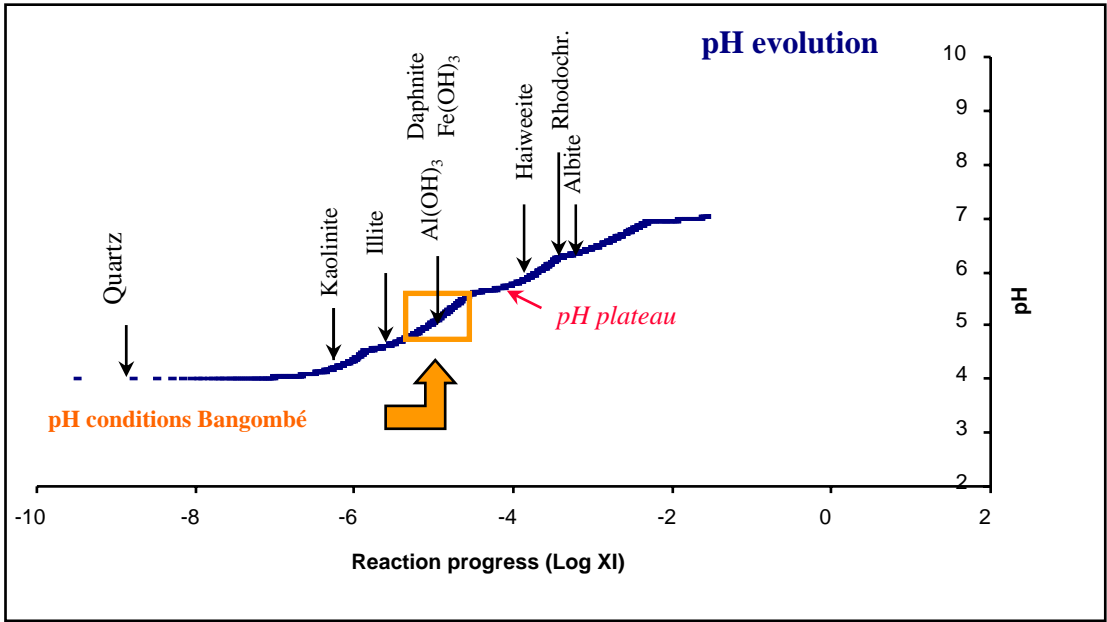
Uranyl-silicates/-phosphates and uranium oxides

←  
←  
**maintained in contact**



Primary minerals suppressed to precipitate

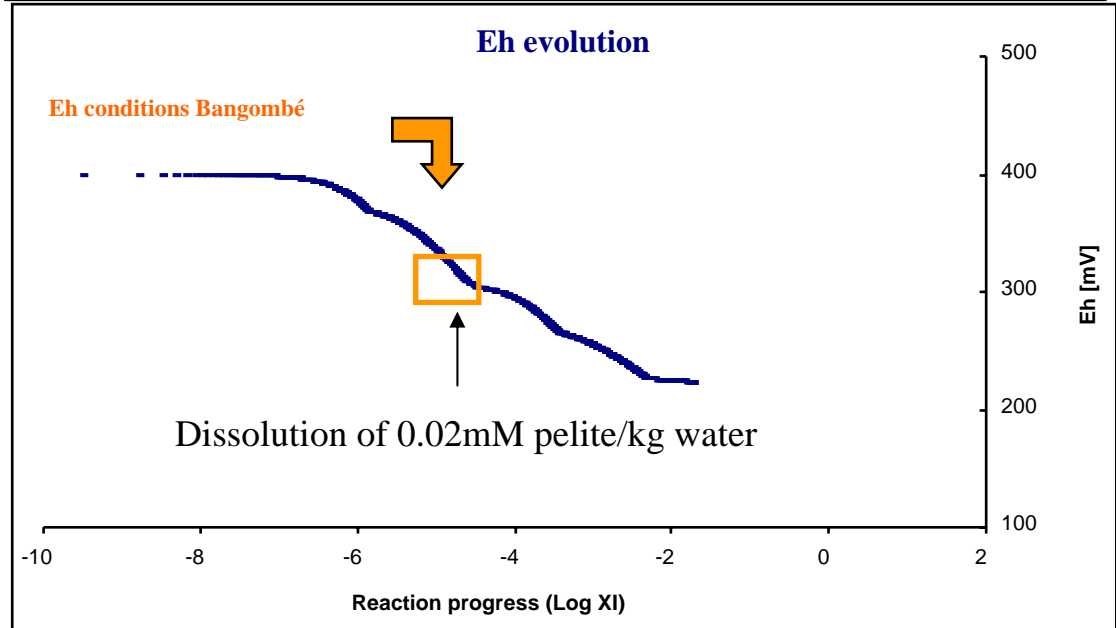
# Results of dissolution test



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

**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)**

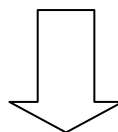
Si, Fe, Mn:	Measured and simulated conc. in the same order of magnitude	
HCO <sub>3</sub> <sup>-</sup> :	Simulated conc. slightly lower than measured values	
K, Na, Al:	Higher than measured values	
<b>U:</b>	<b>41 and 208 µg/L</b>	<b>measured: 33 µg/L</b>

**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

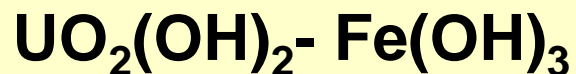
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U-retention in red pelites



**Coprecipitation of U with iron oxides/oxyhydroxides**

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



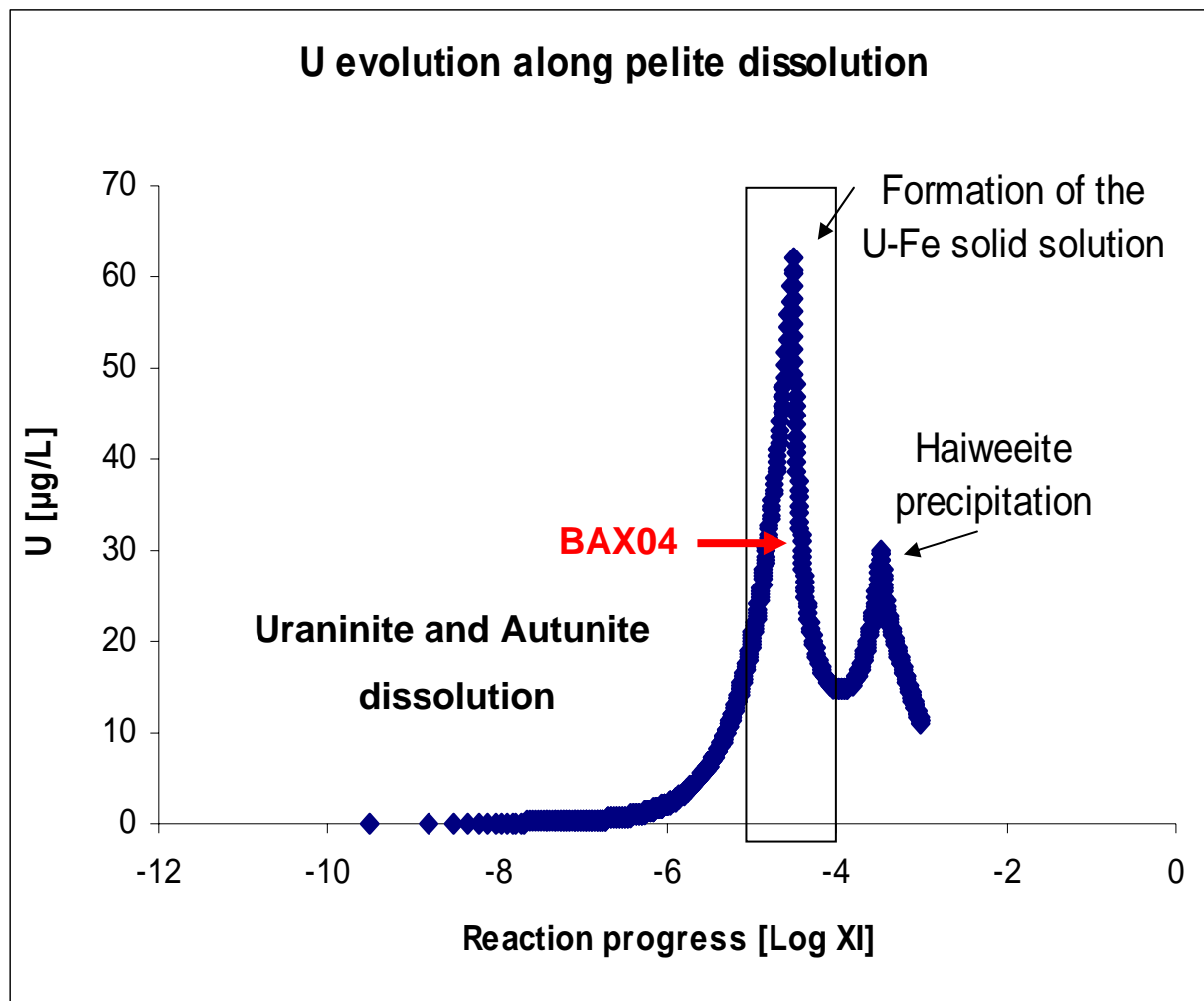
# Results

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

Eh-pH domain BAX04

U = 9 and 44  $\mu\text{g/L}$   
simulated

33  $\mu\text{g/L}$   
measured



# Conclusions

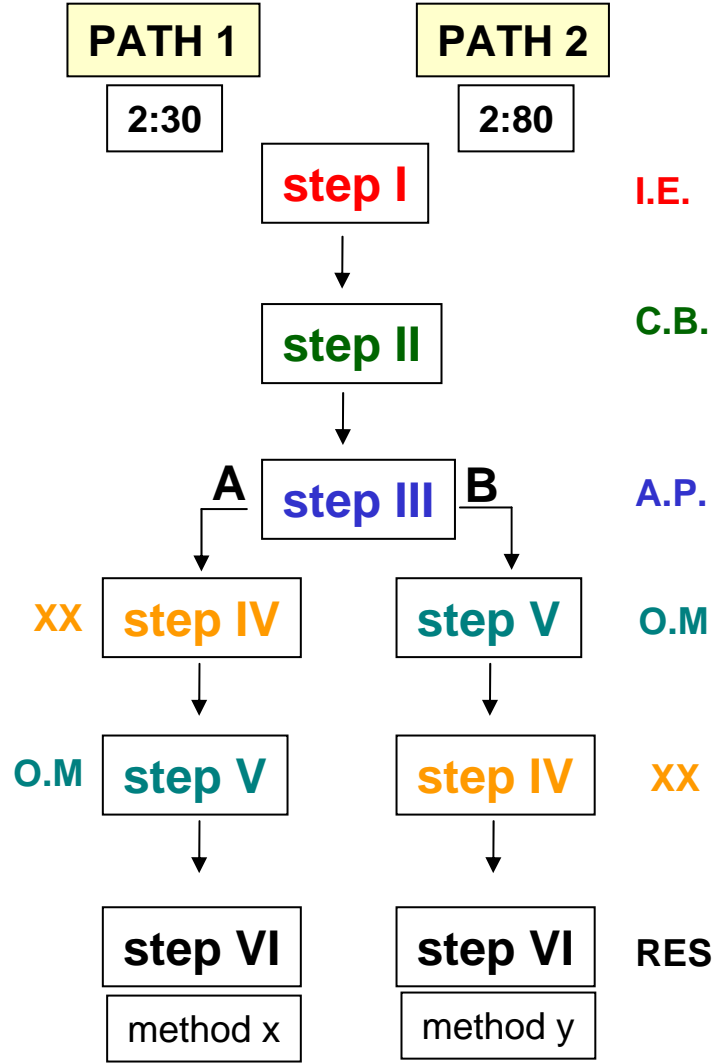
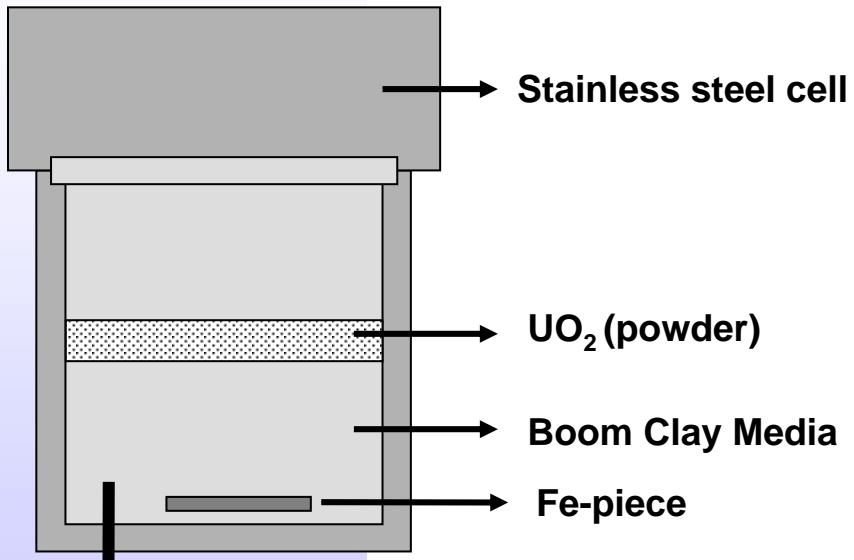
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**The high U-concentrations in the field can be quite well reproduced by assuming only local dissolution of trace amounts of uranium minerals occurring in the red pelites.**

**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  $\alpha$ -doped  $UO_2$  in Boom Clay  
conditions



# Objectives of experimental studies

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**Determine dissolution rates of  $\alpha$ -doped  $\text{UO}_2$  in different Boom clay media**



**Investigate influence of  $\alpha$ -activity on the  $\text{UO}_2$  dissolution rates**



**Get mechanistic understanding of U-retention/migration processes**

# Model validation

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long-term processes



## Numerical model

applicability

limitations



## Laboratory experiments

short-term processes

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

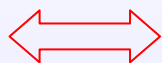
**Thanks for your attention...**





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

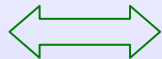
Reactor  
water



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**

**consistent 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**