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New insights on the changes induced by a potential CO_2 leakage on the fate of trace metals in fresh groundwater: The case of the Albian aquifer

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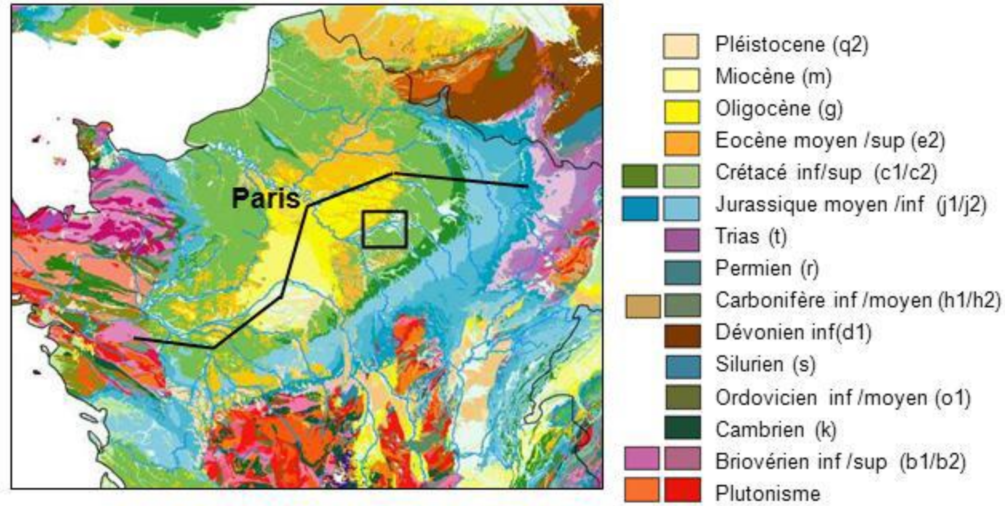
Potentials impacts on GW resources

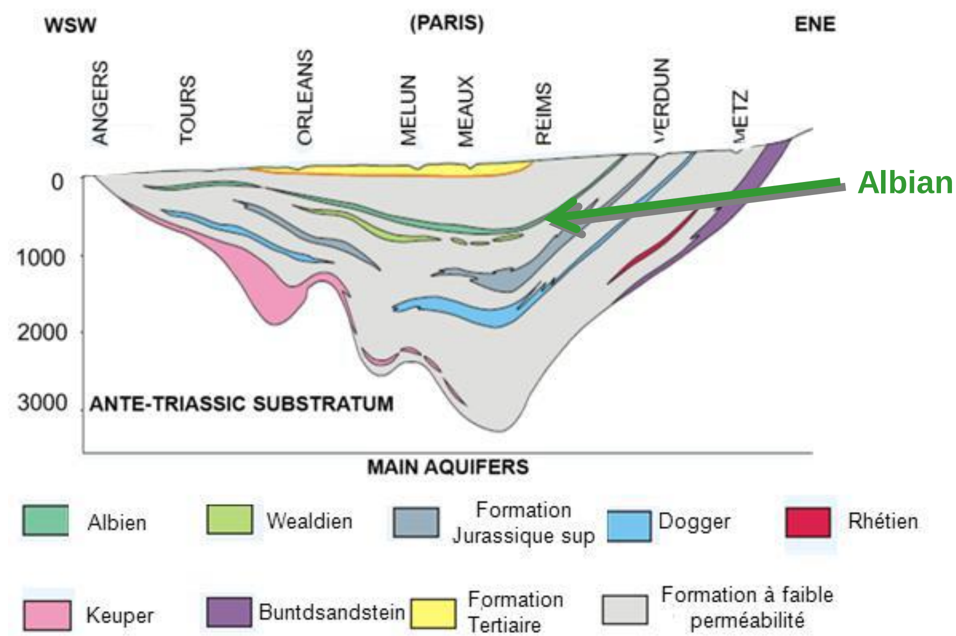
> **CIPRES: French national project dedicated to asses potential impacts of CO_2 leak on GW quality**

> **Identification of the geochemical reactivity**
  - Trace element mobilization

- **Case study: Albian aquifer**
  - Strategic reserve for DW supply
  - Multi-layered aquifer with a specific layer : green sand
    - Glauconite ?

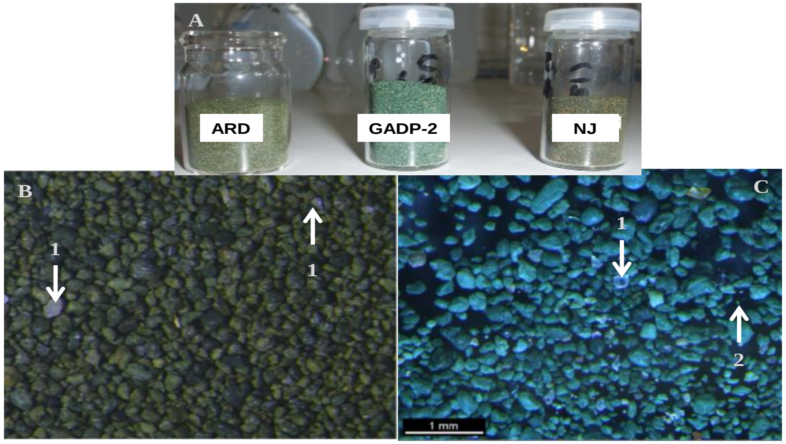
- **Research strategy combining experiments and modelling: 1 step for glauconite + 1 step on Green sand**





Glauconite reactivity: experiments

> **3 glauconites have been studied**
(ARD, GADP-2, NJ)



> **Alteration range**
- GADP-2 < ARD < NJ

> **Isotherms on glauconite (Barsotti et al., 2014)**
- Ni, Zn and As
- 5 concentrations ranging from 10^{-6} to 10^{-4} mol.l^{-1}
- 2 pH: pH 7 and pH 5

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Glauconite reactivity: Modelling surface processes

> A **surface complexation model** associated with a **ion exchange model** (PHRREQC code + Thermoddem databse)

Ion exchange

(Na^+, K^+, H^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+})

$$zXCat_1 + Cat_2{}^{z+} \leftrightarrow zXCat_2 + zCat_1{}^+$$

$$zXCat_1 + M^{z+} \leftrightarrow zXM + zCat_1{}^+$$

+

Surface complexation

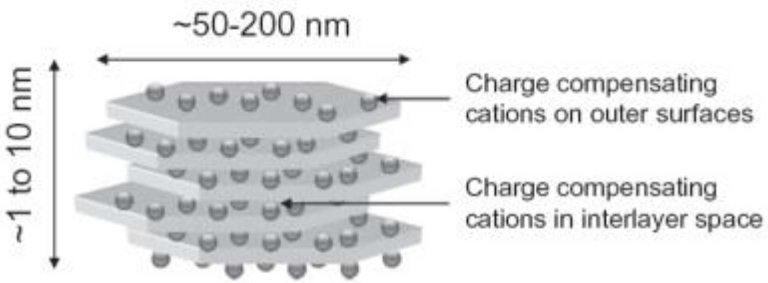
(H^+, Ni^{2+}, Zn^{2+})

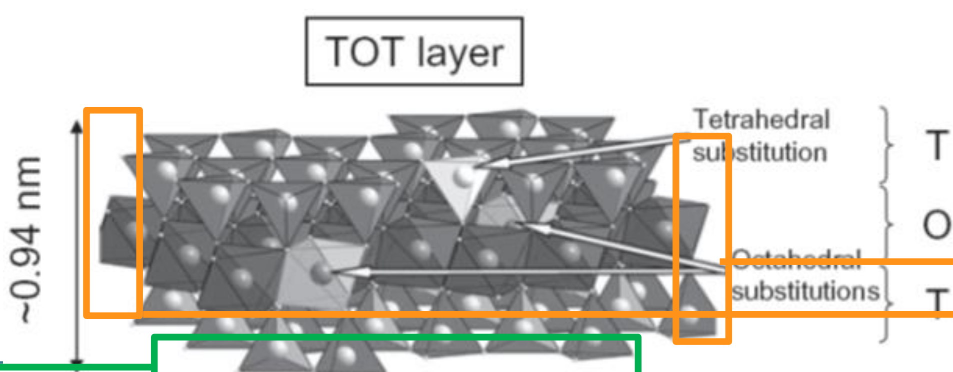
$$>S^- + H^+ \leftrightarrow >SOH$$

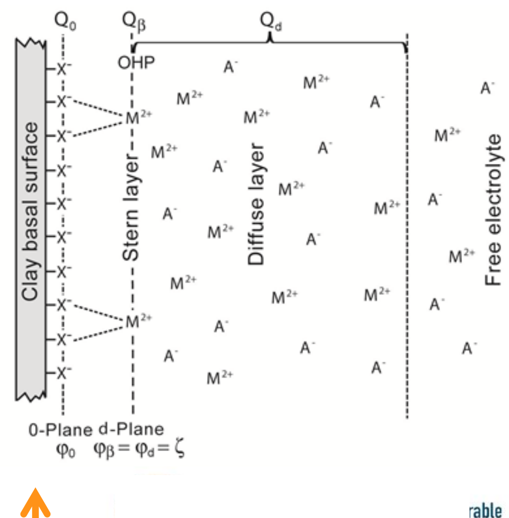
$$>SOH + H^+ \leftrightarrow >SOH_2{}^+$$

$$>2S^- + M^{2+} \leftrightarrow >SO_2M$$

$$>SOH^+ + A^- \leftrightarrow >SOH_2A$$







Glauconite reactivity: Results

> **Ni is more sorbed than Zn**

> **Less altered glauconite has higher affinity towards Zn and Ni**

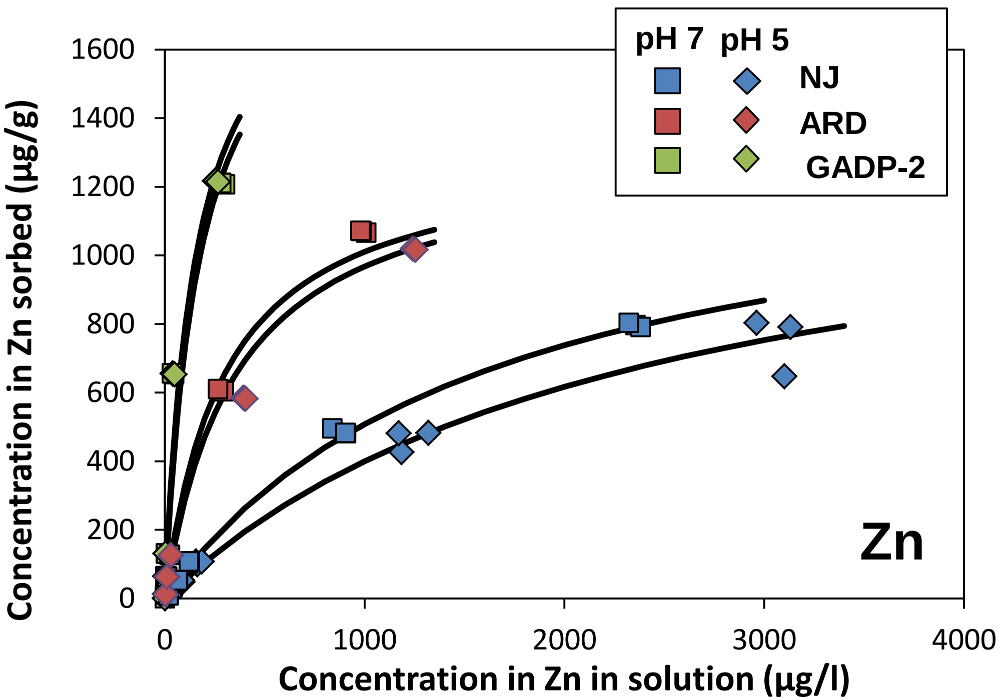
- GADP-2 > ARD > NJ

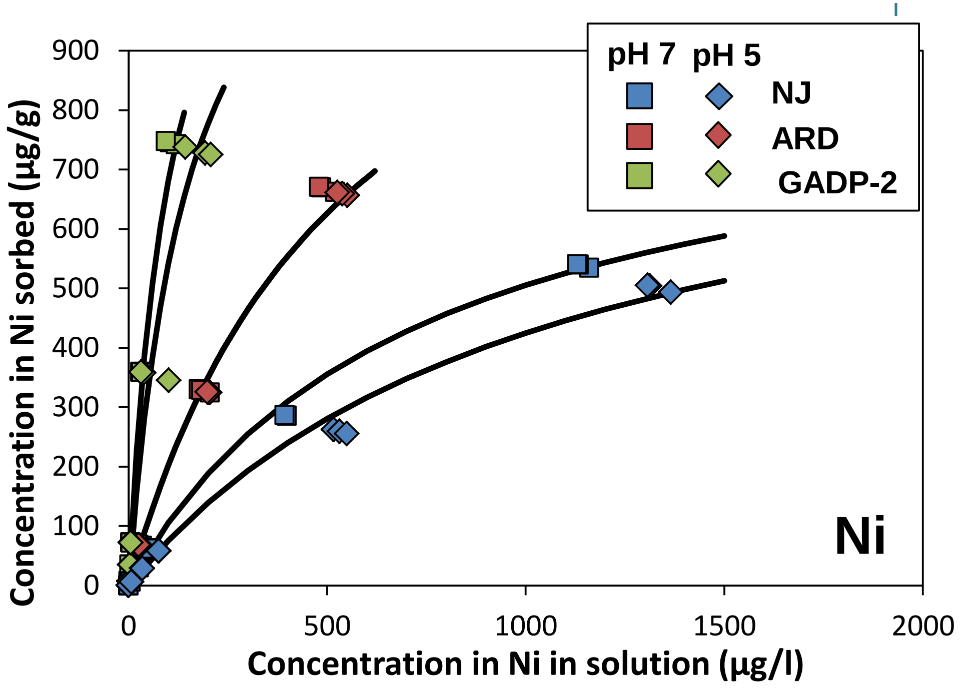
> **Surface properties are contrasted according to alteration of glauconite**

- CEC and specific surface area are higher for GADP-2 and ARD

> **Lower sorption under acidic conditions**

- Surface sites are mainly protonated: SOH_2^+



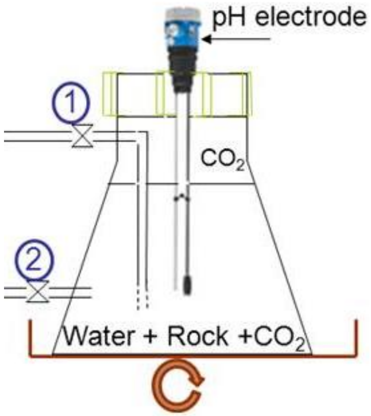


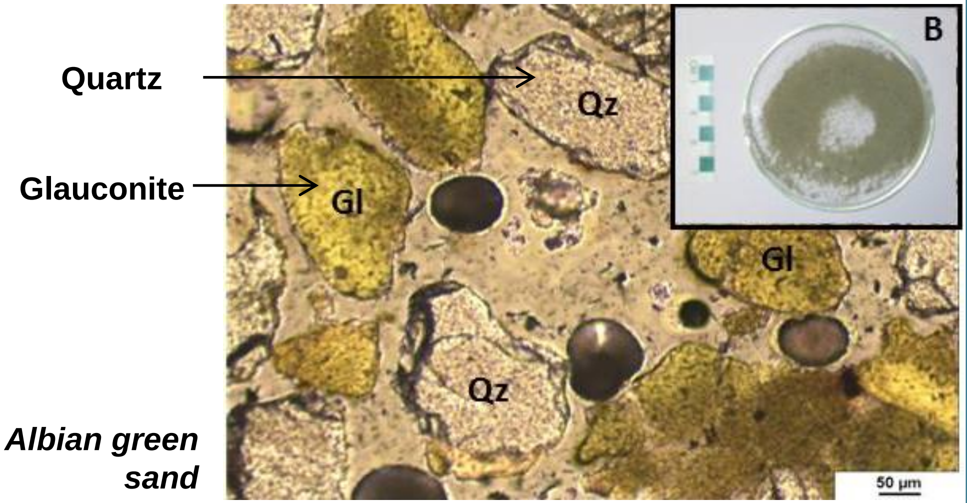
Green sand: Batch experiments (Humez et al., 2012)

> **Green sand + Albian water + 2 bars CO_2**

> **1 month length (1d, 7d, 14d, 30d)**
- Evidence for fast and slow release of trace metals

> **Parameters:**
- pH
- redox,
- major elements
- trace elements





Albian green sand

Green sand: Geochemical model

(Phreeqc code + Thermoddem database)

Minerals	Fraction
Quartz	0,8
Glauconite	0,1
Kaolinite	0,098
Fluorapatite	0,001
Calcite	0
Sidérite	0

> Mineralogical assemblage

- Primary minerals: Qz, Glauconite, Dolomite, Fluorapatite
- Secondary minerals: calcite, siderite,

> Initial water

- Equilibrium with primary minerals

> Geochemical processes

- Kinetic dissolution/precipitation reactions for primary minerals (TST formalism)

$$R_m = k_m A_m \left[\exp\left(\frac{p\Delta_r G}{RT}\right) - 1\right]^q = k_m A_m \left[1 - \left(\frac{Q_m}{K}\right)^p\right]^q$$

- Equilibrium dissolution/precipitation reactions for secondary minerals
- SCM to simulate sorption on quartz
- SCM + CE model to simulate sorption on glauconite (step 1)

Green sand: Results

> **pH decreases and alkalinity increases**

- CO_2(g) dissociation

$$H_2CO_3 \leftrightarrow CO_3^{2-} + 2H^+$$

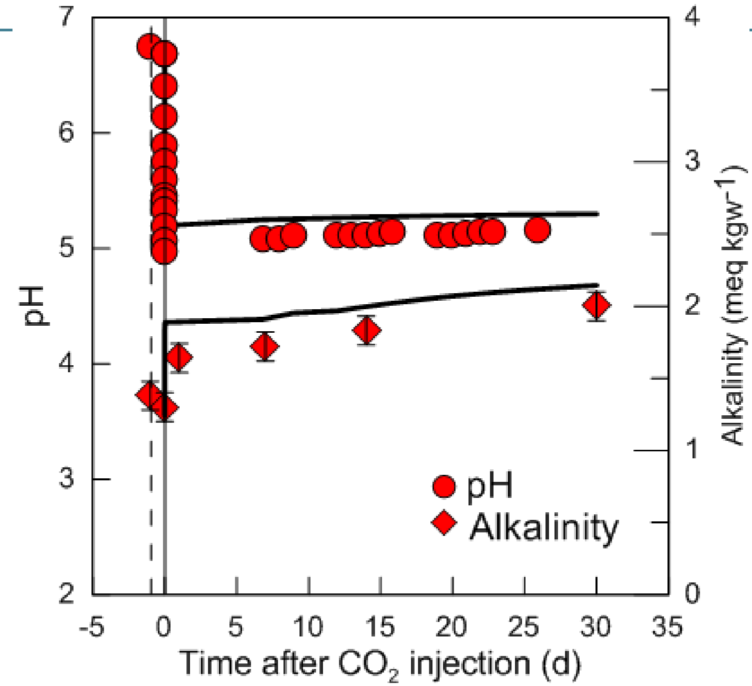
- The decrease of pH is buffered by dolomite dissolution

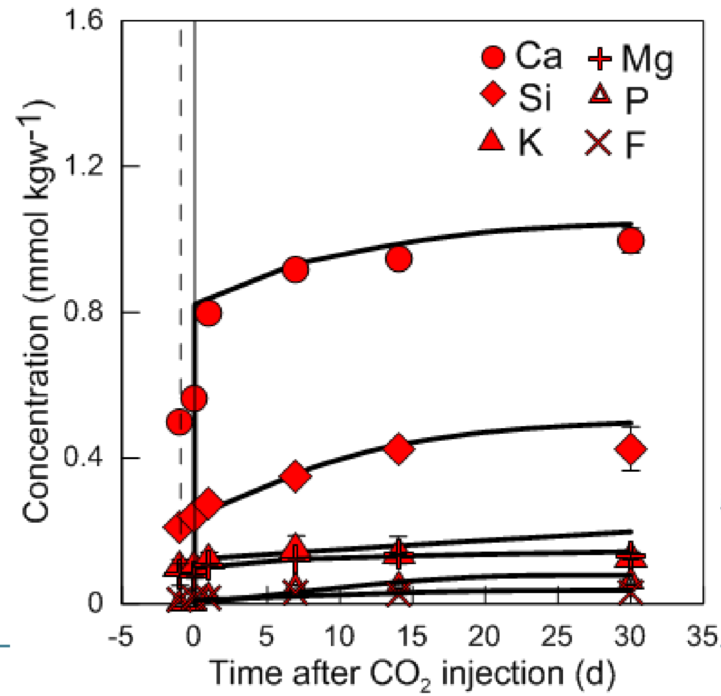
$$CaMg(CO_3)_2 + 2H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + H_2CO_3$$

- Dolomite dissolution increases alkalinity

> **Si and K increases caused by glauconite dissolution reaction**

> **Dolomite and fluorapatite induces an increase of Ca, Mg and PO4 concentrations**





Green sand: Results

> **Increase of the Zn and Ni concentrations.**

- pH decrease.

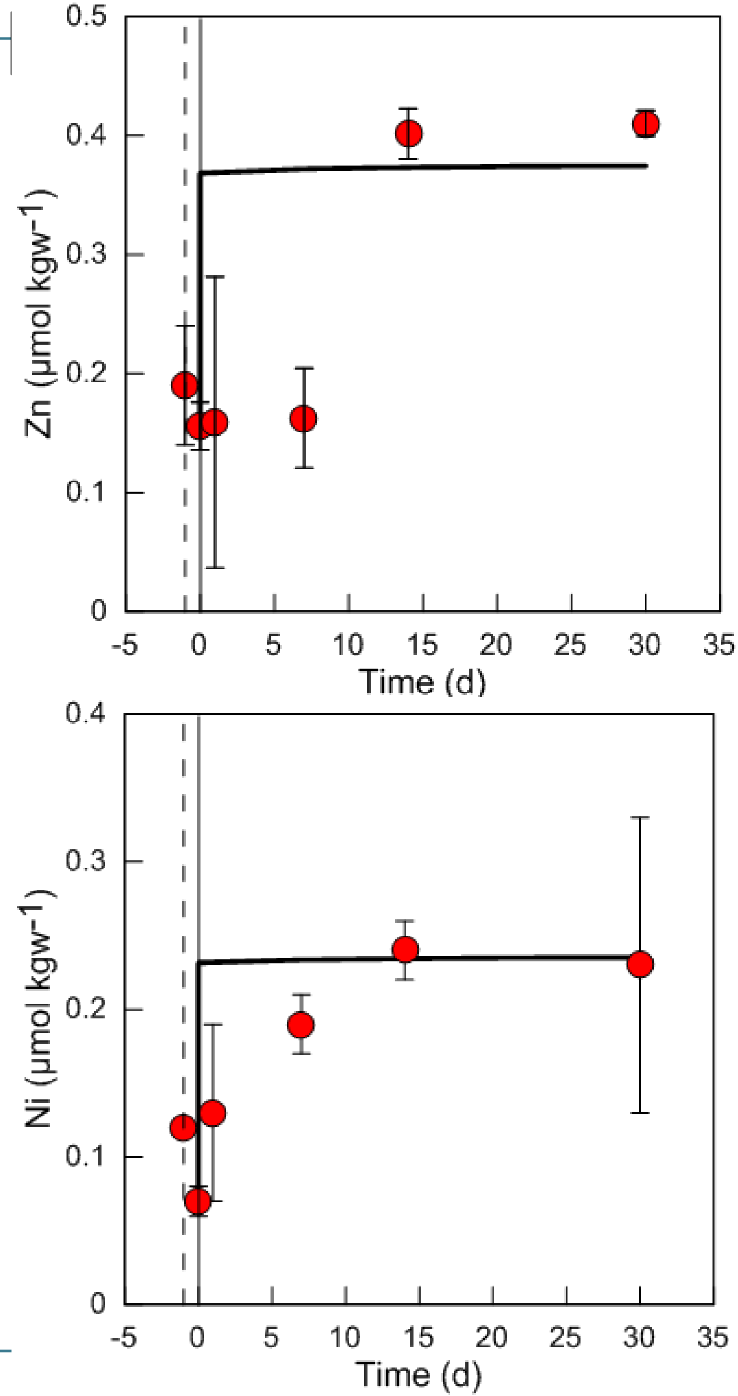
$$SO_2M + 2H^+ \leftrightarrow 2SOH + M^{2+}$$

- Competition with the desorbed Ca and Mg

$$X_2M + Ca^{2+} \leftrightarrow X_2Ca + M^{2+}$$

$$X_2M + Mg^{2+} \leftrightarrow X_2Mg + M^{2+}$$

- Dissolution of glauconite induces a decrease of reactive surface area



Conclusions

> **Understanding glauconite reactivity towards trace metals**

- Strong reactivity for Zn and Ni
- pH-dependence of sorption processes
- Both edge surface site and basal surface sites are involved

> **Geochemical model developed to simulate how CO2 leakage could impact release of trace metal in Albian green sand**

- pH, alkalinity and fate of main major elements are correctly reproduced
- Release of Zn and Ni is accurately simulated
- Sorption reactions are strongly impacted by CO2 leakage

> **Predictive 3D reactive transport model to extrapolate geochemical variability with time and space according to flow rate and leakage rate (poster n° 1598)**

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Thank you for your attention

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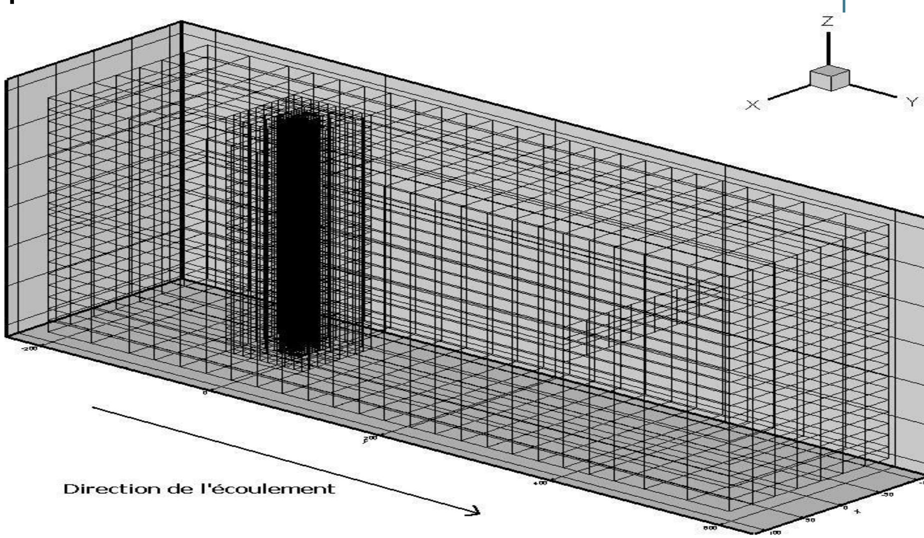
Step 3: 3D Reactive transport model

> **3D reactive transport model: ThoughReact version 3 (Xu, 2010)**
- Geocehmical model based on step 2 (React code)
- Tough code for flow and transport models
- Thermodynamic database Thermoddem (Blanc et al. 2012)
- Homogeneous system

> **Geometry**
- 200 m x 500 m and 60 m thick
- Grid refinement around the leaking point

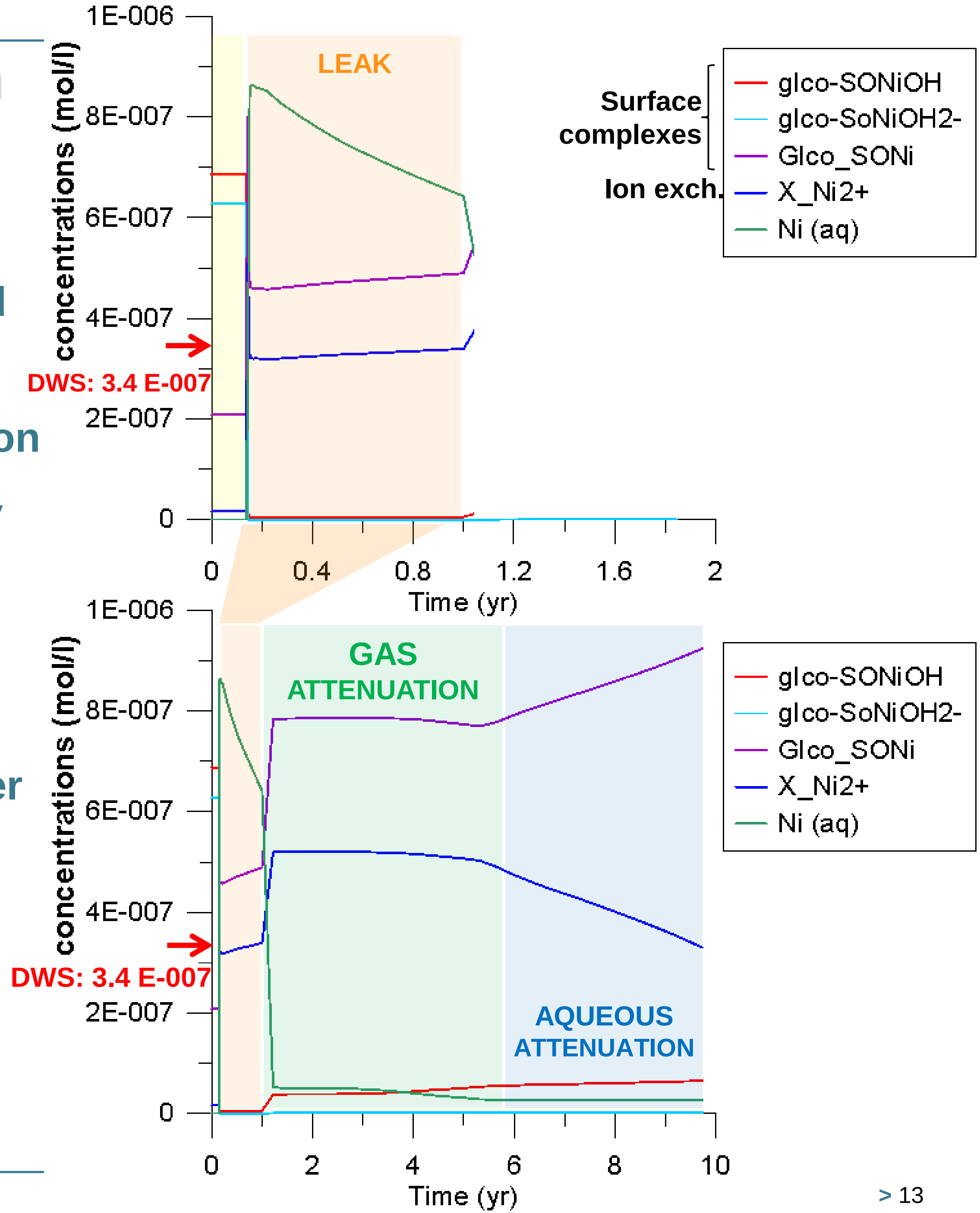
> **Simulation (100 years)**
- CO_2 leak at the bottom 3 rates

> **Scenario**
- Initial equilibrium (50 d)
- CO_2 leak (315 d.)
- natural release (99 yr)



Step 3: Nickel evolution with time at the leaking point

- Initial conditions Ni sorbed onto glauconite
- CO_2 leak induced desorption of Ni from glauconite: Ni aqueous concentration ↗
- Ni re-sorption after stop of CO_2 leakage
- More details given in poster n°1598



Step 2: Experimental studies on the albian green sand

> **Batch reactor (Humez et al. 2012)**

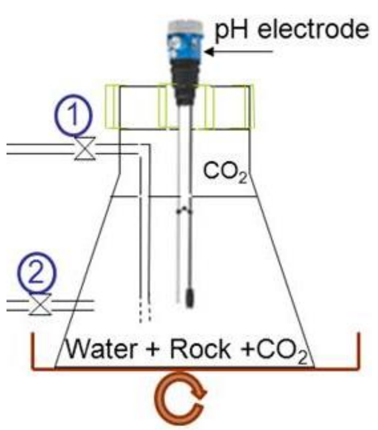
- Evidence of surface reaction (fast release) and mineral dissolution (slow release) in presence of CO_2

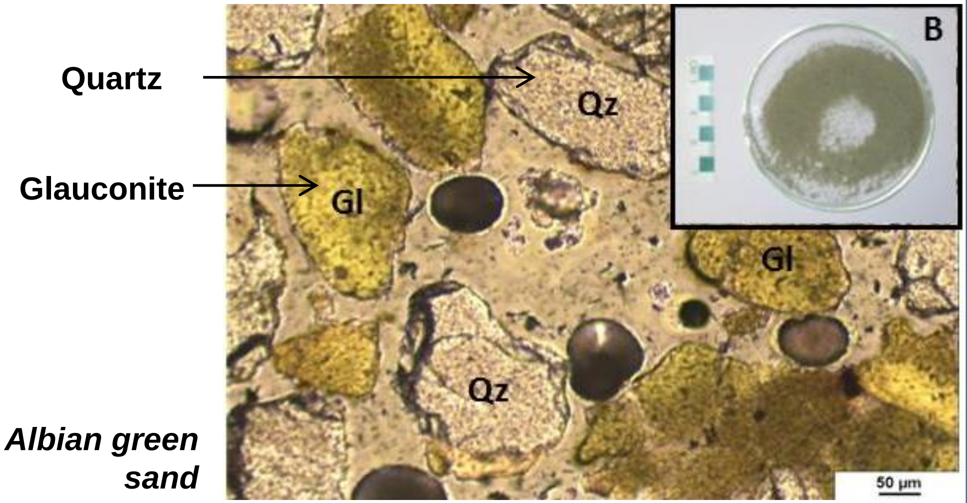
> **Isotherms on glauconite (Barsotti et al. 2014)**

- Ni, Zn and As

> **Geochemical model (PHREEQC)**

- Kinetics parameter for mineral dissolution
- Surface processes





Albian green sand

Expérimentations

> Echantillons

> Caractérisation des glauconites

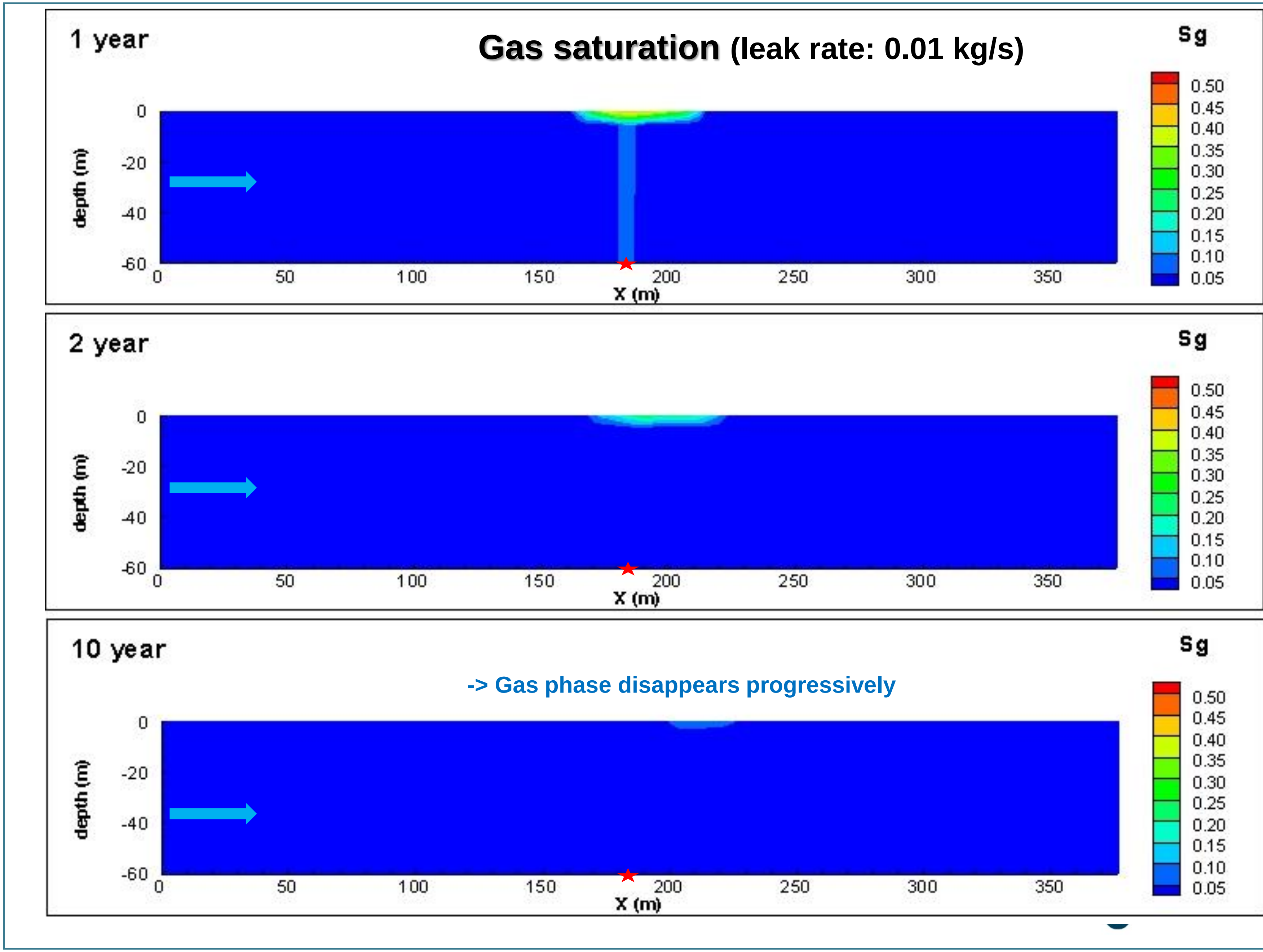
- Minéralogie des roches (DRX, MEB, analyse chimiques)
- Lames minces (MEB, µsonde électronique)
- Mesures de la CEC
- Mesures surface spécifique (BET)

> Isothermes d'adsorption

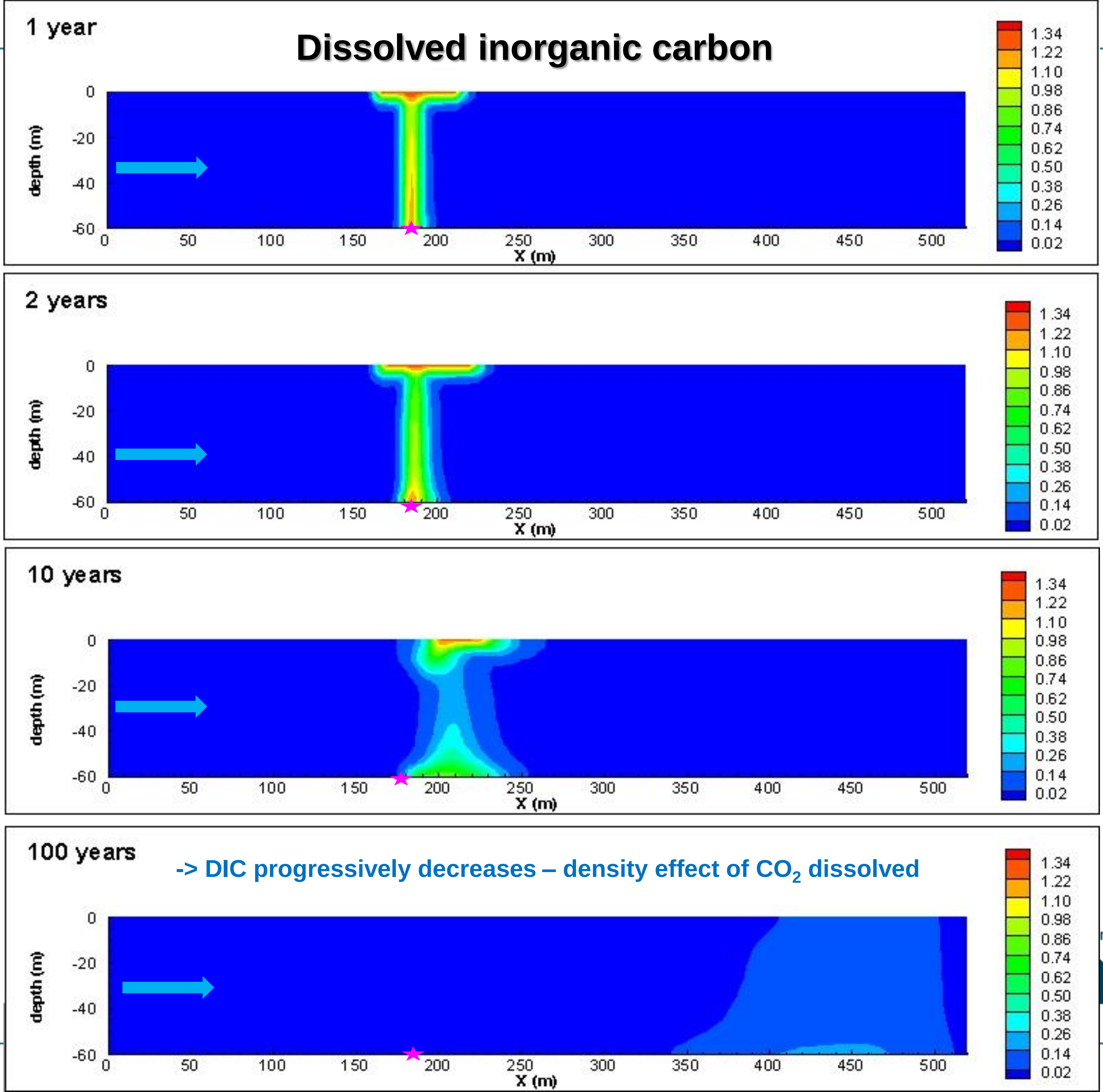
- 3 ETM sélectionnés: Zn, Ni, As
- 5 concentrations initiales croissantes:

Zn ($1x10^{-6}$ à $1x10^{-4}$ $mol.l^{-1}$), Ni ($5x10^{-7}$ à $5x10^{-5}$ $mol.l^{-1}$) et As ($5x10^{-6}$ à $5x10^{-4}$ $mol.l^{-1}$)

- 2 pH: pH 7 (pH de l'eau de l'Albien) et pH 5 (pH eau + fuite de CO_2)

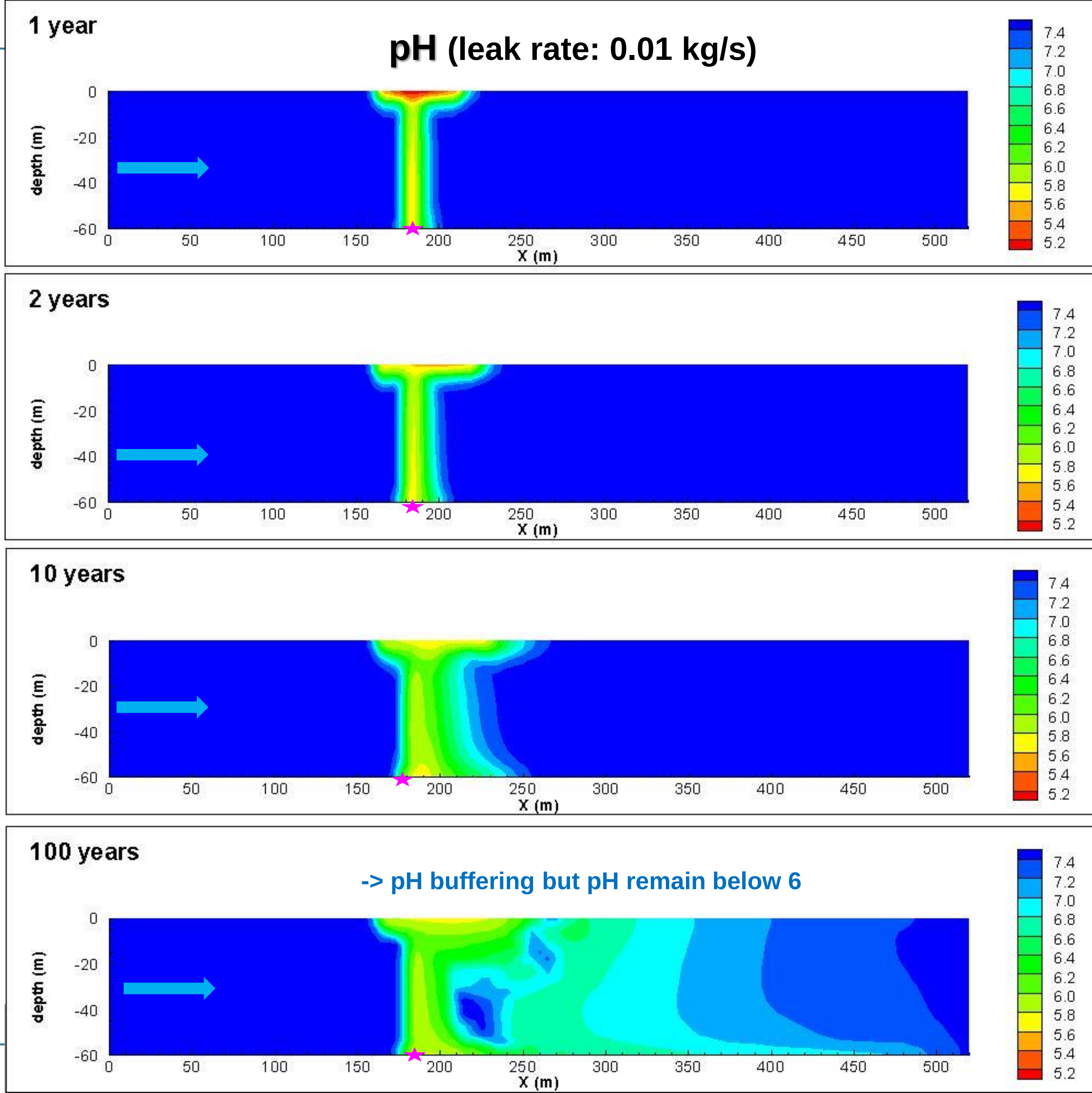

Gas saturation (leak rate: 0.01 kg/s)
1 year
2 year
10 year
-> Gas phase disappears progressively
Sg
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
depth (m)
0
-20
-40
-60
0
50
100
150
200
250
300
350
X (m)

Dissolved inorganic carbon

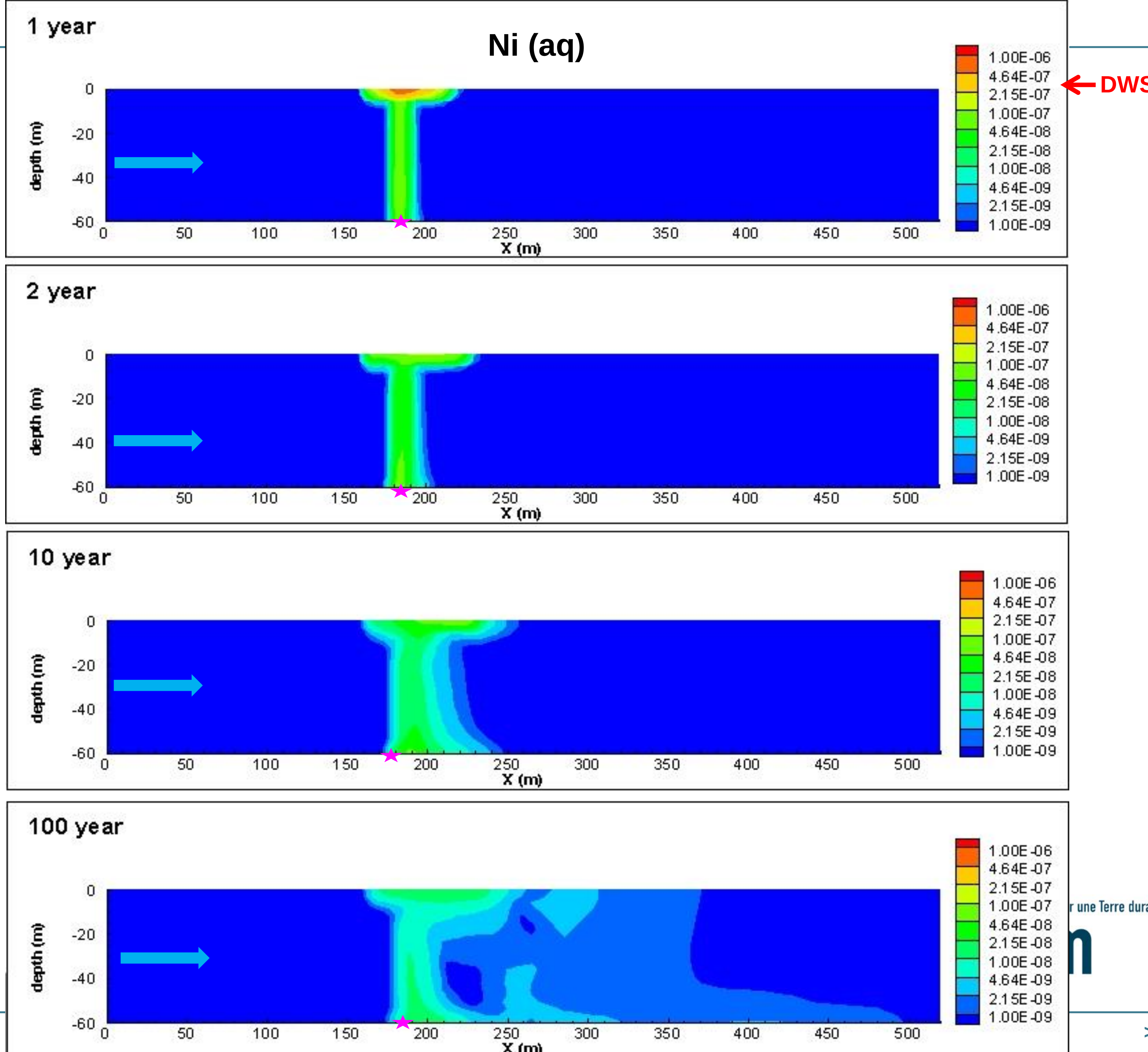


-> DIC progressively decreases – density effect of CO_2 dissolved

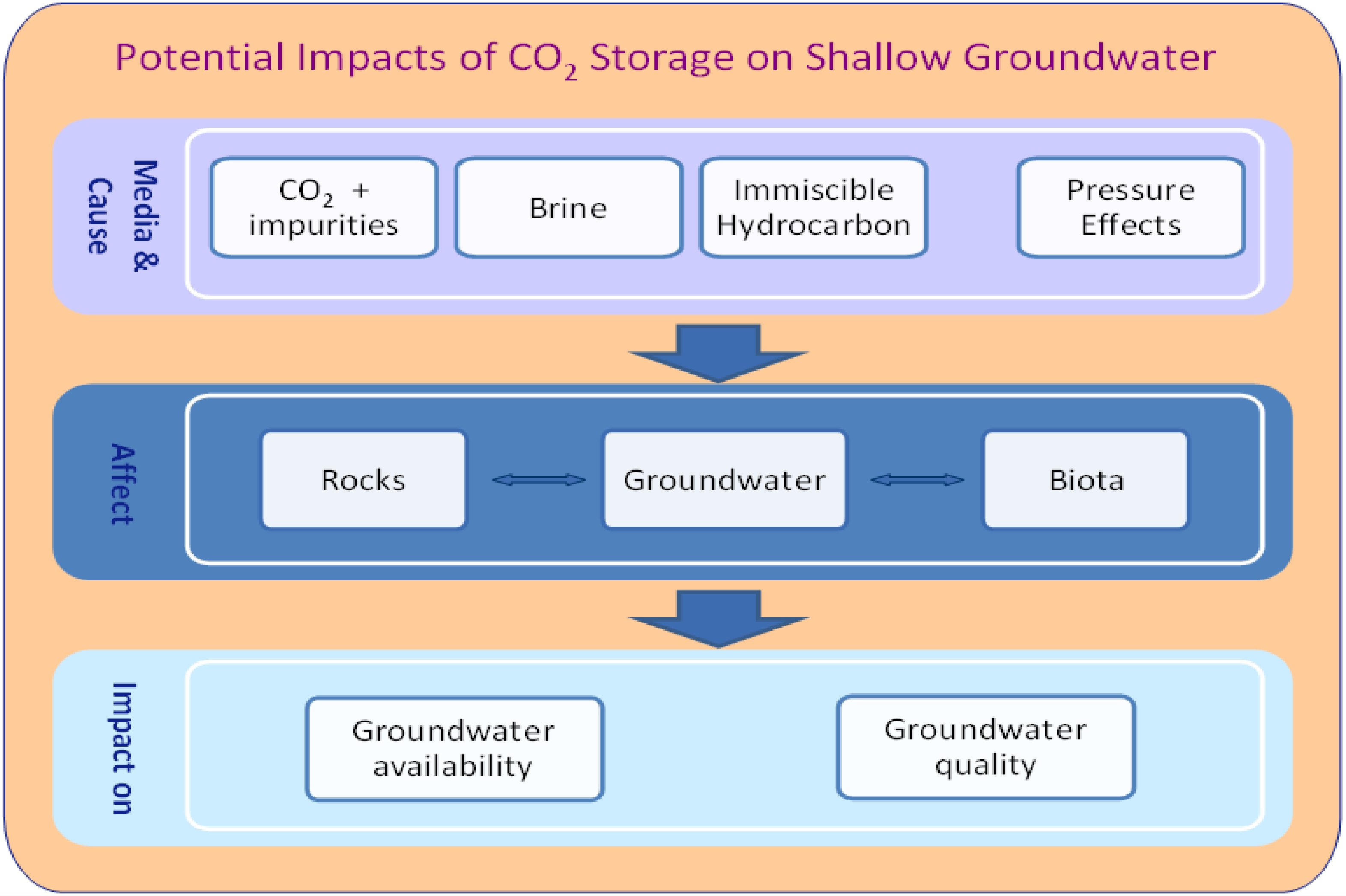
pH (leak rate: 0.01 kg/s)



-> pH buffering but pH remain below 6


Ni (aq)
1 year
2 year
10 year
100 year
depth (m)
0
-20
-40
-60
X (m)
0
50
100
150
200
250
300
350
400
450
500
1.00E-06
4.64E-07
2.15E-07
1.00E-07
4.64E-08
2.15E-08
1.00E-08
4.64E-09
2.15E-09
1.00E-09
DWS

Potentials impacts on GW resources

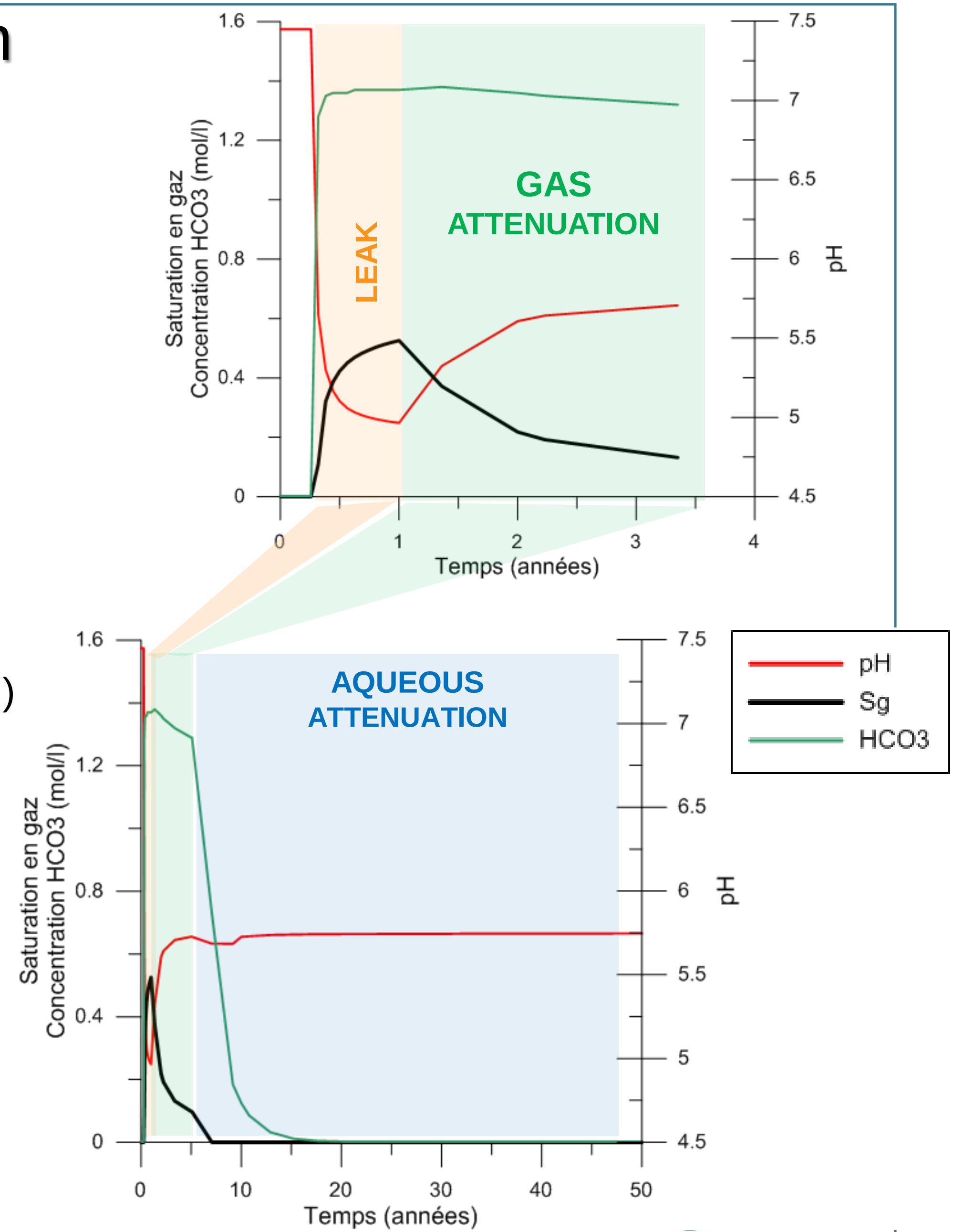


Geochemical evolution with time at the leaking point
(leak: 0.01 kg/s for 315 d.)

> CO_2 leak
- Sg increase to 0.18 and 0.5 at top
- pH drop from 7.5 to 4.9
- DIC increase from 0.002 to 1.3 mol/l

> Attenuation of gas phase
- Sg drop to 0 (migration & dissolution)
- DIC nearly constant ~1.3 mol/l
- pH increase to 5.6

> Attenuation of aqueous species
- DIC progressively decrease
- pH smoothly increase up to 5.8



Geochemical monitoring

> Some criteria

- Position & depth
  - Sensors & sampling must intercept the plume
- Parameters & leakage indicators
  - Early warning (fast reaction)
  - Conservative vs natural attenuation (long term)
- Baseline & threshold values
  - Significant variation of monitored values vs. initial value (background level and natural variation) :

    Variation (Δ) > natural variability

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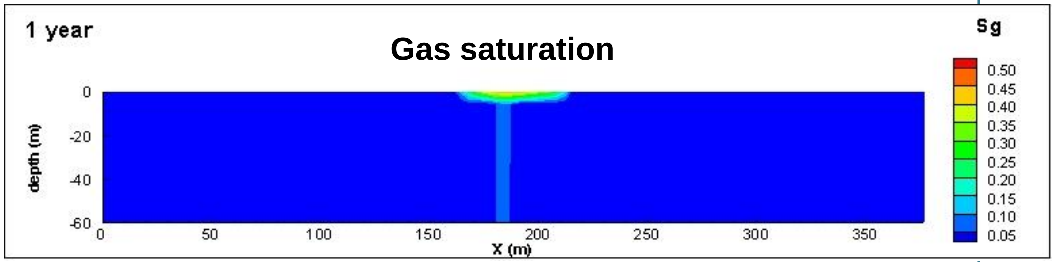
Geochemical monitoring

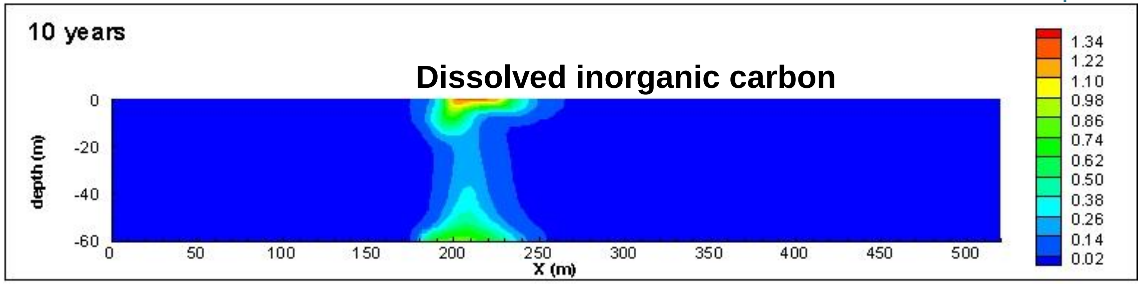
> Gas phase

- Above the leak
- Accumulation at the top of the aquifer
- Natural attenuation after leak stops
  - 7 yrs above the leak



> Dissolved CO_2

- Above the leak
- At the top of the aquifer



- Long term: vertical migration (density effect) and accumulation at the bottom
- Δ10% : at 100 m downstream in 10 yrs (earlier than pH)
- Natural attenuation after leak stops
  - 22 yrs above the leak

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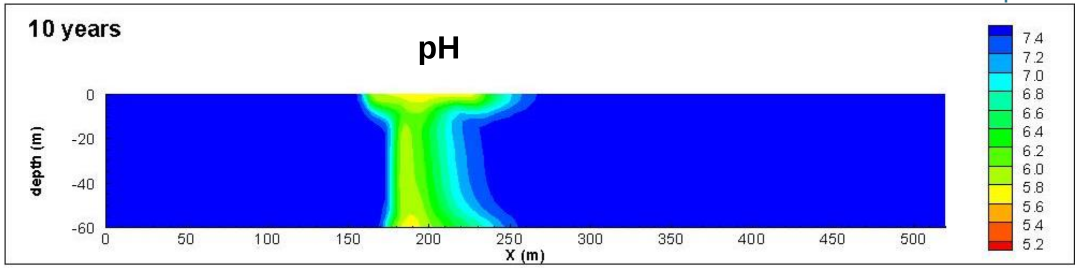
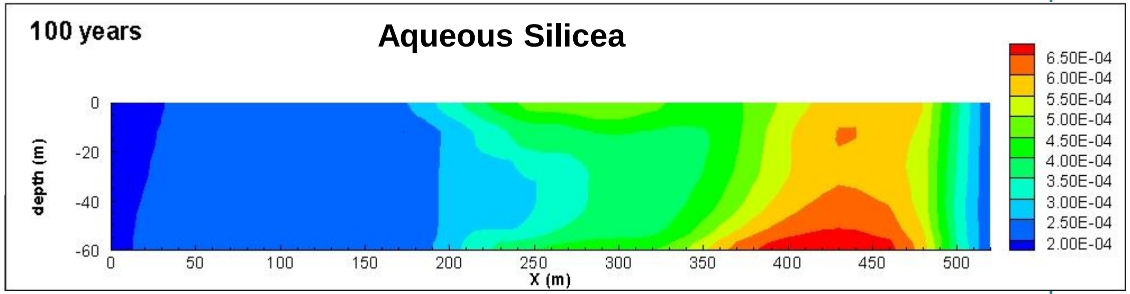
Geochemical monitoring

> pH

- First detection above the leak & <u>at the top</u>
- Long term : vertical migration (density effect) and acidification <u>at the bottom</u>
- Limited natural buffering effect: pH ~6
- Δ10% : at 100 m downstream in 30 yrs





> Aqueous Silica

- Dependant of pH drop
- First detection above the leak & a<u>t the top</u>
- Long term (kinetic control, glauconite dissolution): accumulation <u>with time</u>
- Δ10% : at 100 m downstream in 12 yrs (earlier than pH)
- No natural attenuation after leak stops

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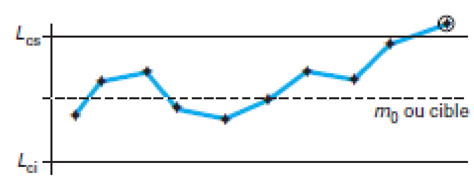
Baseline acquisition and monitoring

Steps	Regional investigation	Exploration	Installation	Exploitation		Post-closure Monitoring	After transfer of repsonsability
Objectives	Identify area suitable for CCS	Identify and characterize the reservoir suitable (security) for CCS	Installation and equipment	Injection of CO_2		Control and monitoring of the storage	Permanent confinement of the storage
Monitoring	**Environmental Baseline**	**Monitoring plan design**	**Operational Baseline acquisition**	**Regular Monitoring**	**Reinforced Monitoring**	**Post-exploitation monitoring**	**Long term monitoring**
Target	State of the art Spatial variability	Identify the risk and define an adapted monitoring plan	Baseline acquisition for the designed monitoring plan Temporal variability	Monitoring and threshold values to trigger reinforced monitoring	In case of anomalous value during baseline monitoring, identify any failure	Post-exploitation monitoring	Long term monitoring
Time	> 2 yrs	~ 5 yrs	**> 2 yrs**	20-50 yrs		20-50 yrs	20-50 yrs



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Conclusions

> **Impacts assessment and elaboration of monitoring plan need to consider correctly the geochemical reactivity of CO_2**
- In this case study: 272 t injected during 1 yr, CO_2 plume migrates 30 m downstream and disappear in 7 yrs (regional flow enhance natural attenuation)
- Vertical migration (↑↓) and down-gradient (with regional flow)
- Density effect observed directly (gas, DIC) but also on water composition and geochemical reactivity

> **Different geochemical reactivities with time and space according to flow rate and leakage rate**
- This dynamic must be considered in monitoring plan (parameters, localization)
  - 3 areas: gas plume, CO_2 footprint, down-gradient area
  - 3 steps : leakage, gas saturation decrease, aqueous attenuation
- Natural system are heterogeneous -> complex flow & pathways

> **Metal release and scavenging**
- Metals are released (exceeding DWS according to leakage rate) but released Ni and Zn are rapidly sorbed
- Sorption (ion exchange and surface complexes) along the CO_2 plume pathway is sensitive to pH variations

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Transport model

> Simplified properties

- Homogeneous aquifer
- Porosity 20% and permeability 500 mD
- Sleipner sand properties for the multiphase flow (unconsolidated sandy formation analogue)

> Regional flow

- Based on observed values
  - No hydraulic gradient = 0
  - Hydraulic gradient = 4‰ (2 bar / 500 m)

Relative permeability (van Genuchten)	**From Sleipner (Utsira sandstone)**
$\lambda=1-1/n$	0.63
Residual liquid phase Saturation (Slr)	0.05
Liquid phase saturation (Sls)	1
Irreductible gas saturation (Sgr)	0.2
Capillarity pressure (van Genuchten)	
$\lambda=1-1/n$	0.63
Residual liquid phase saturation (Slr)	0.05
Po (Pa)	1400
Liquid phase saturation (Sls)	1

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Geochemical model

> Primary minerals

- observed experimentally and included in the models (with kinetics)
  - Qz, Glauconite, Kaol, Fluorapatite, Pyrite
  - Reactive surface area optimized
    - Exp. surf. area / 1000

> Initial water

- Initial water is equilibrated with minerals
- Initial water is slightly under-saturated with secondary minerals
  - calcite and siderite

Minerals	Fraction
Quartz	0,8
Glauconite	0,1
Kaolinite	0,098
Fluorapatite	0,001
Pyrite	0,001
Calcite	0
Sidérite	0

	Bouligny	Orsay	Model
pH	6.6	7.5	**7.5**
pCO_2 (bar)	0.023	0.004	**0.004**
Al (mol/l)	4.78×10^{-8}	9.27×10^{-8}	**5.63×10^{-9}**
C (mol/l)	2.17×10^{-3}	2.02×10^{-3}	**2.03×10^{-3}**
Ca (mol/l)	5.0×10^{-4}	7.1×10^{-4}	**4.87×10^{-4}**
Cl (mol/l)	1.38×10^{-4}	1.38×10^{-4}	**1.38×10^{-4}**
F (mol/l)	1.05×10^{-5}	1.05×10^{-5}	**1.05×10^{-5}**
Fe (mol/l)	1.02×10^{-4}	3.04×10^{-6}	**1.22×10^{-5}**
K (mol/l)	1.13×10^{-4}	2.10×10^{-4}	**2.83×10^{-3}**
Mg (mol/l)	1.48×10^{-4}	2.51×10^{-4}	**2.05×10^{-4}**
Na (mol/l)	1.39×10^{-4}	2.44×10^{-4}	**1.39×10^{-4}**
Si (mol/l)	2.08×10^{-4}	2.20×10^{-4}	**1.99×10^{-4}**

Nickel evolution with time at the leaking point

> Initial distribution of Ni

- Aqueous: ε
- Exchange-Ni: +
- Surface complexes: +++

> CO_2 leak

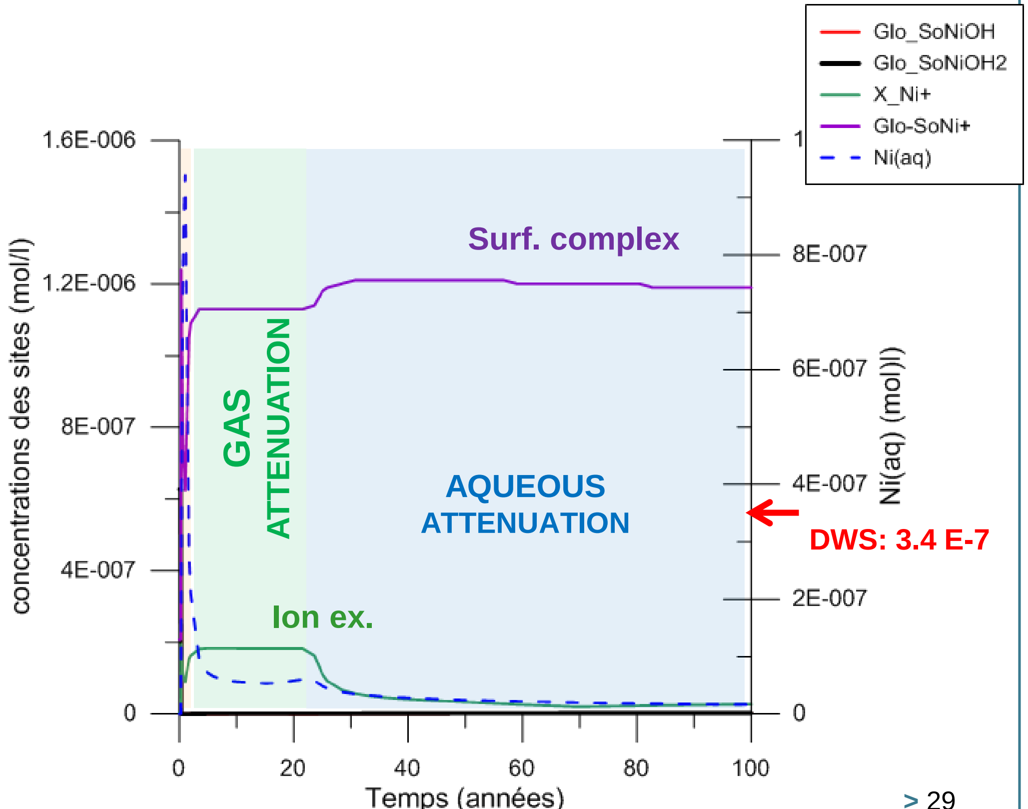
- Aqueous Ni: fast release
  - ⟶ above DWS
- Exchange-Ni: ++
- Surface complexes: +++

> Attenuation of gas phase

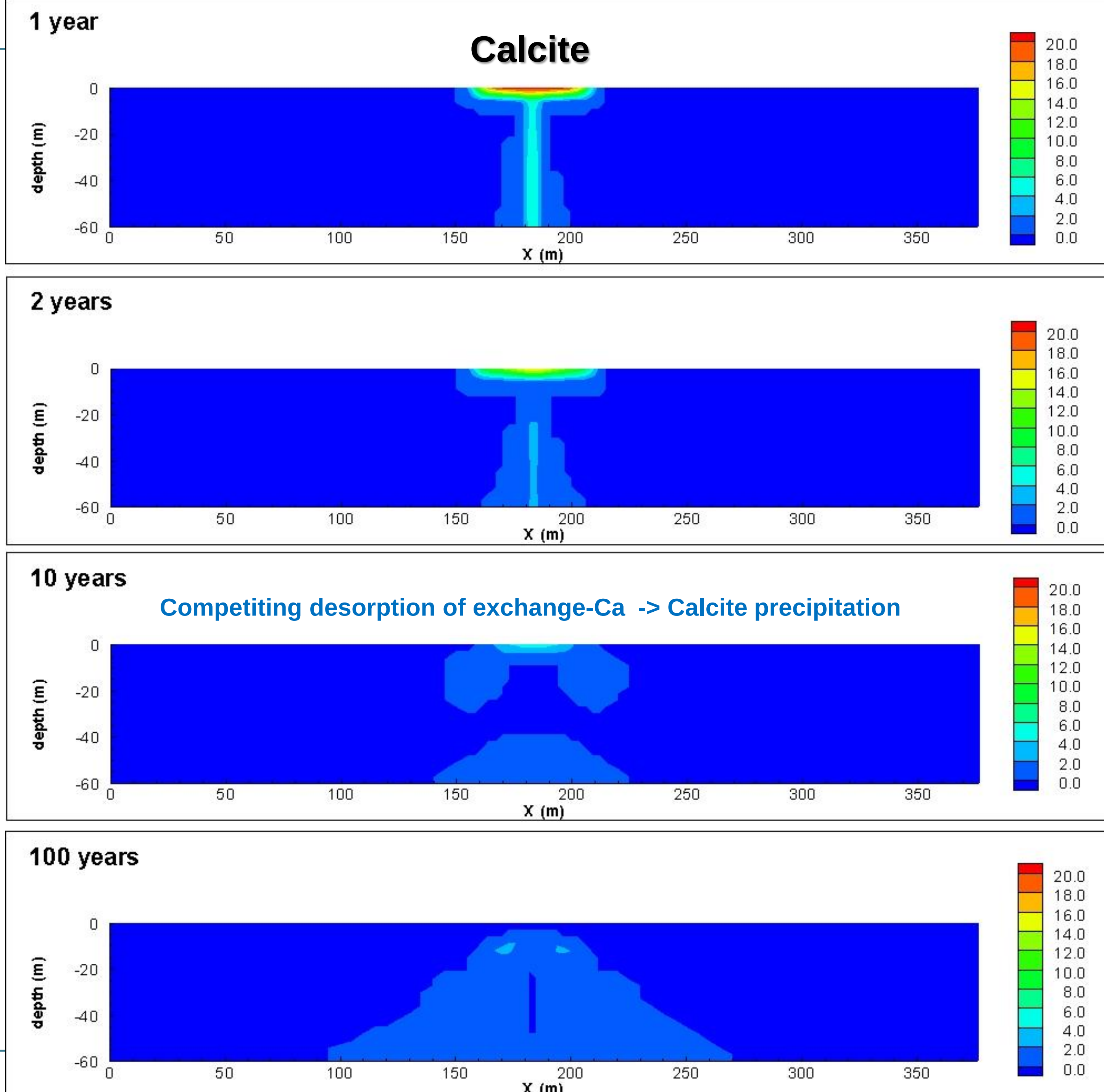
- Aqueous Ni: +
- Exchange-Ni: +++
- Surface complexes: ++++

> Attenuation of aqueous species

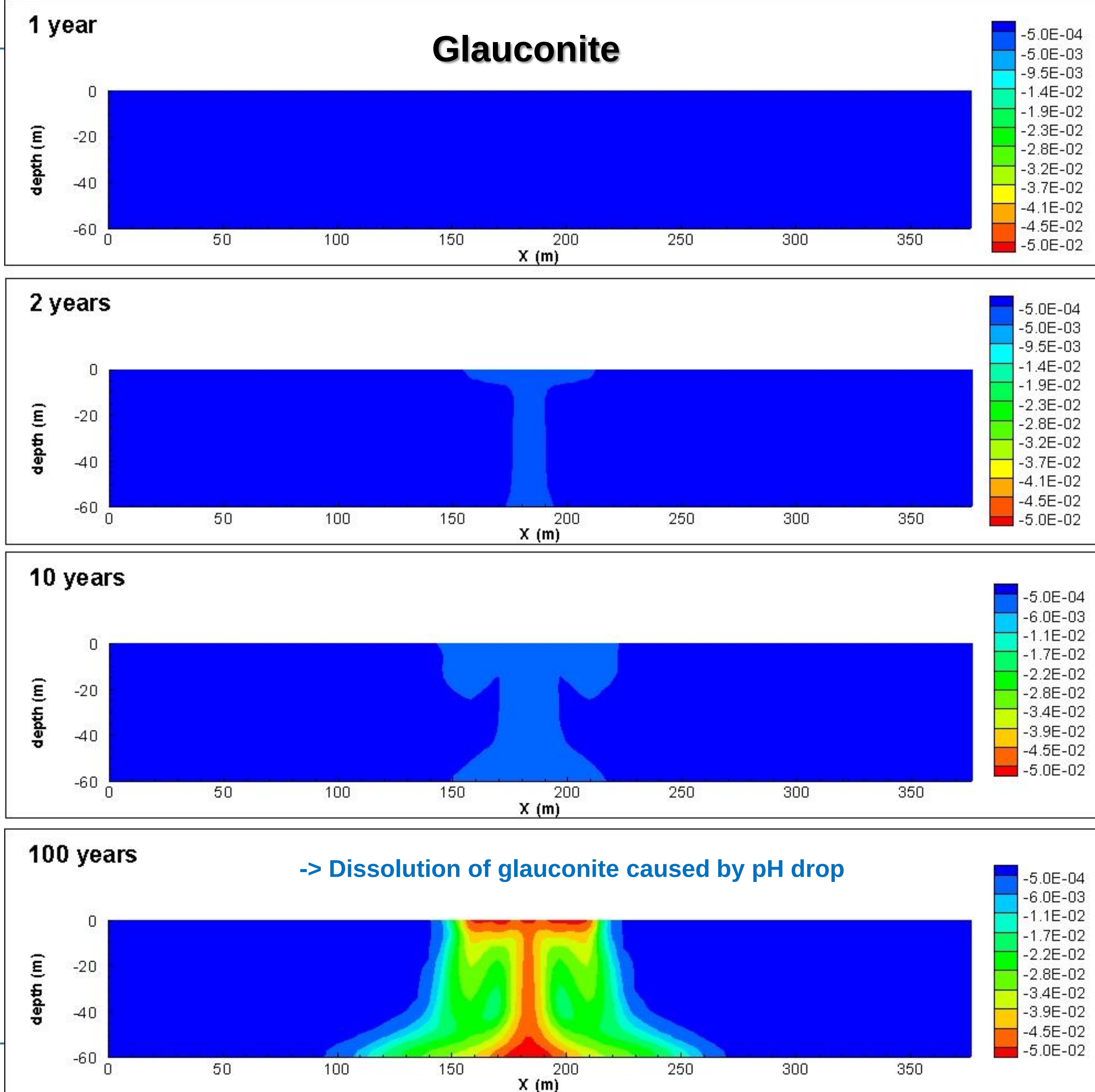
- Exchange-Ni: ++
- Surface complexes: ++++
- Aqueous Ni: ε



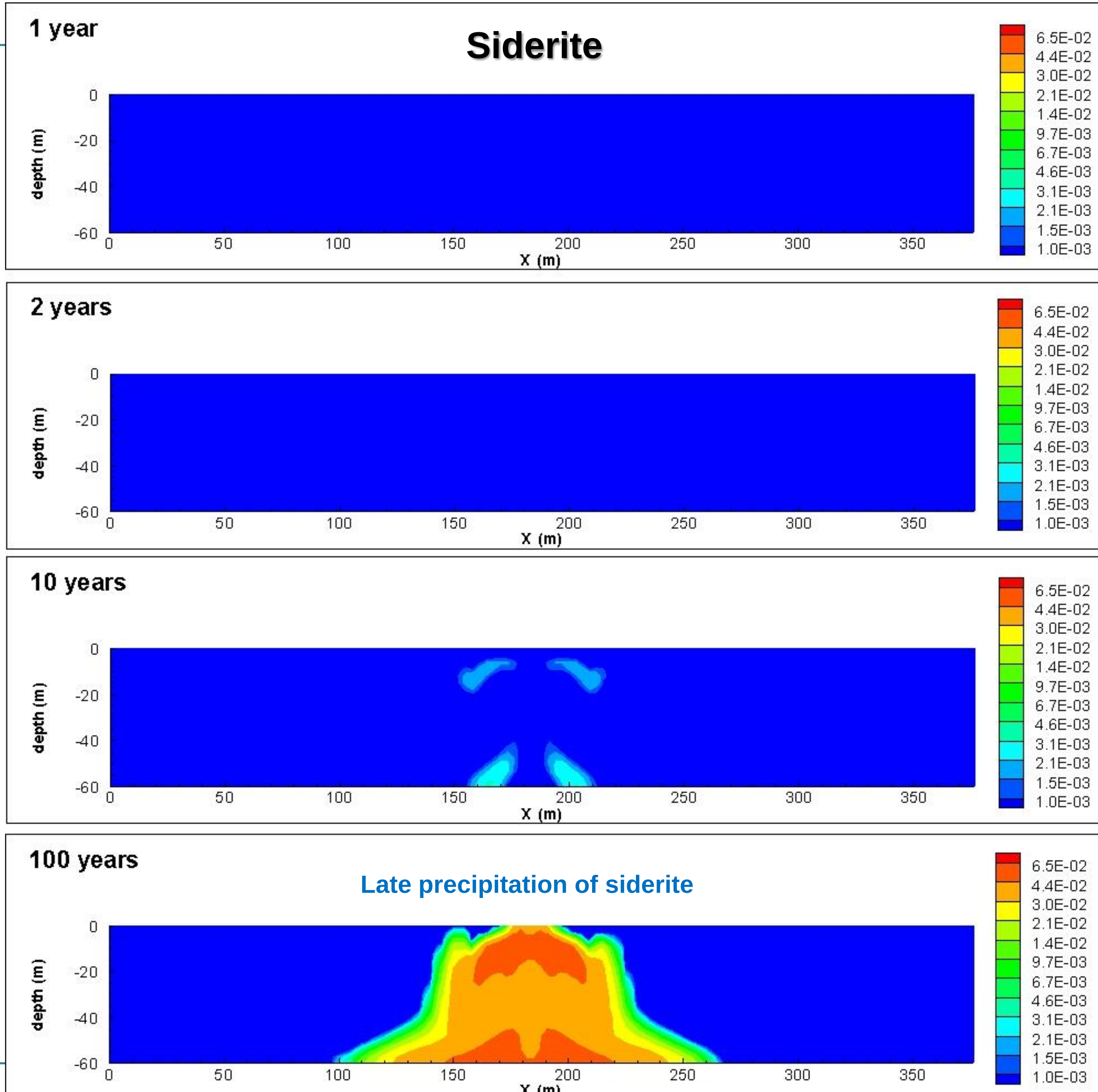
Calcite



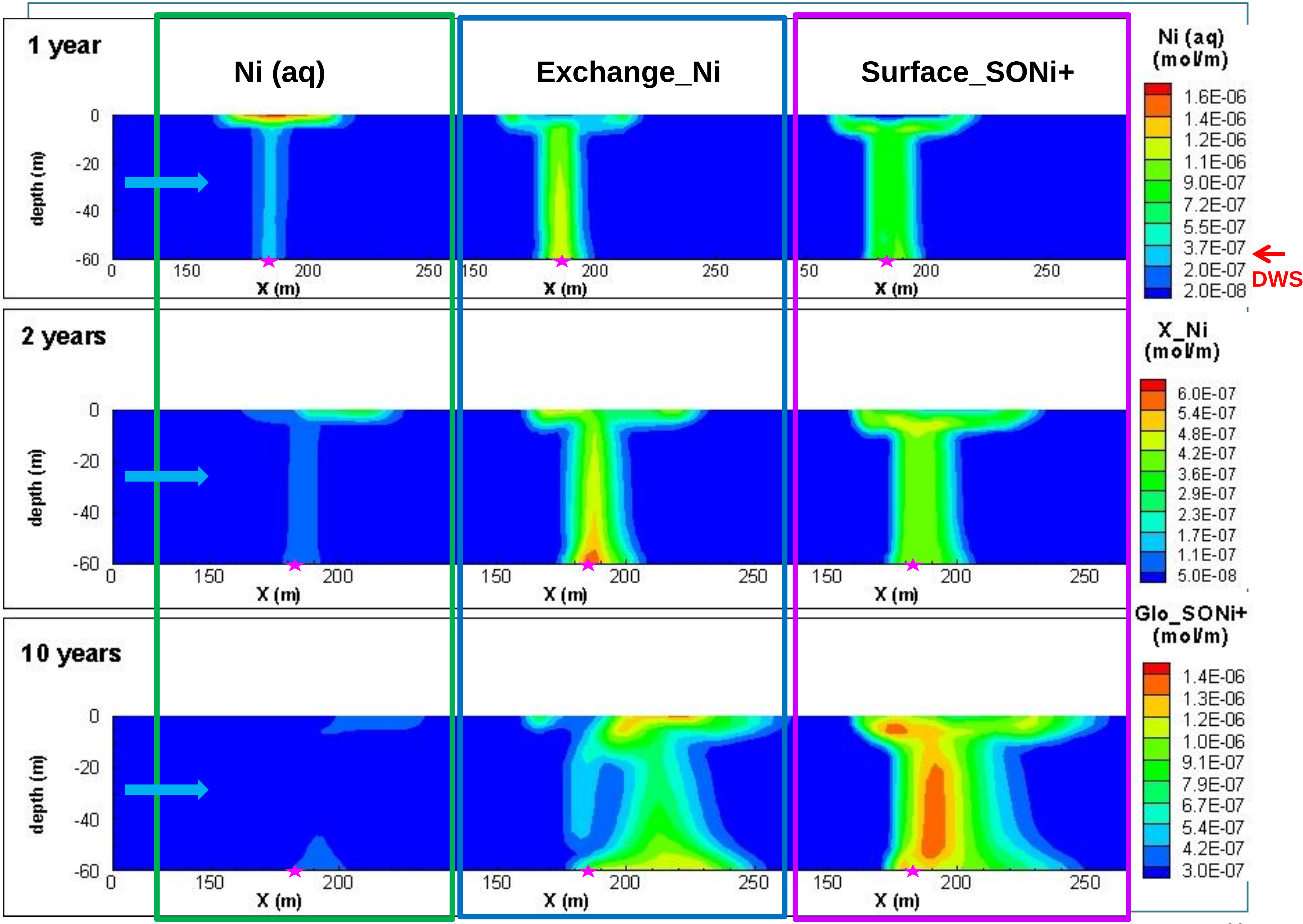
Competititing desorption of exchange-Ca -> Calcite precipitation



Glauconite
1 year
2 years
10 years
100 years
-> Dissolution of glauconite caused by pH drop
depth (m)
0
-20
-40
-60
X (m)
0
50
100
150
200
250
300
350
-5.0E-04
-5.0E-03
-9.5E-03
-1.4E-02
-1.9E-02
-2.3E-02
-2.8E-02
-3.2E-02
-3.7E-02
-4.1E-02
-4.5E-02
-5.0E-02
-5.0E-04
-6.0E-03
-1.1E-02
-1.7E-02
-2.2E-02
-2.8E-02
-3.4E-02
-3.9E-02
-4.5E-02
-5.0E-02



pour une Terre durable



1 year
2 years
10 years
Ni (aq)
Exchange_Ni
Surface_SONi+
depth (m)
X (m)
Ni (aq)
(mol/m)
1.6E-06
1.4E-06
1.2E-06
1.1E-06
9.0E-07
7.2E-07
5.5E-07
3.7E-07
2.0E-07
2.0E-08
DWS
X_Ni
(mol/m)
6.0E-07
5.4E-07
4.8E-07
4.2E-07
3.6E-07
2.9E-07
2.3E-07
1.7E-07
1.1E-07
5.0E-08
Glo_SONi+
(mol/m)
1.4E-06
1.3E-06
1.2E-06
1.0E-06
9.1E-07
7.9E-07
6.7E-07
5.4E-07
4.2E-07
3.0E-07

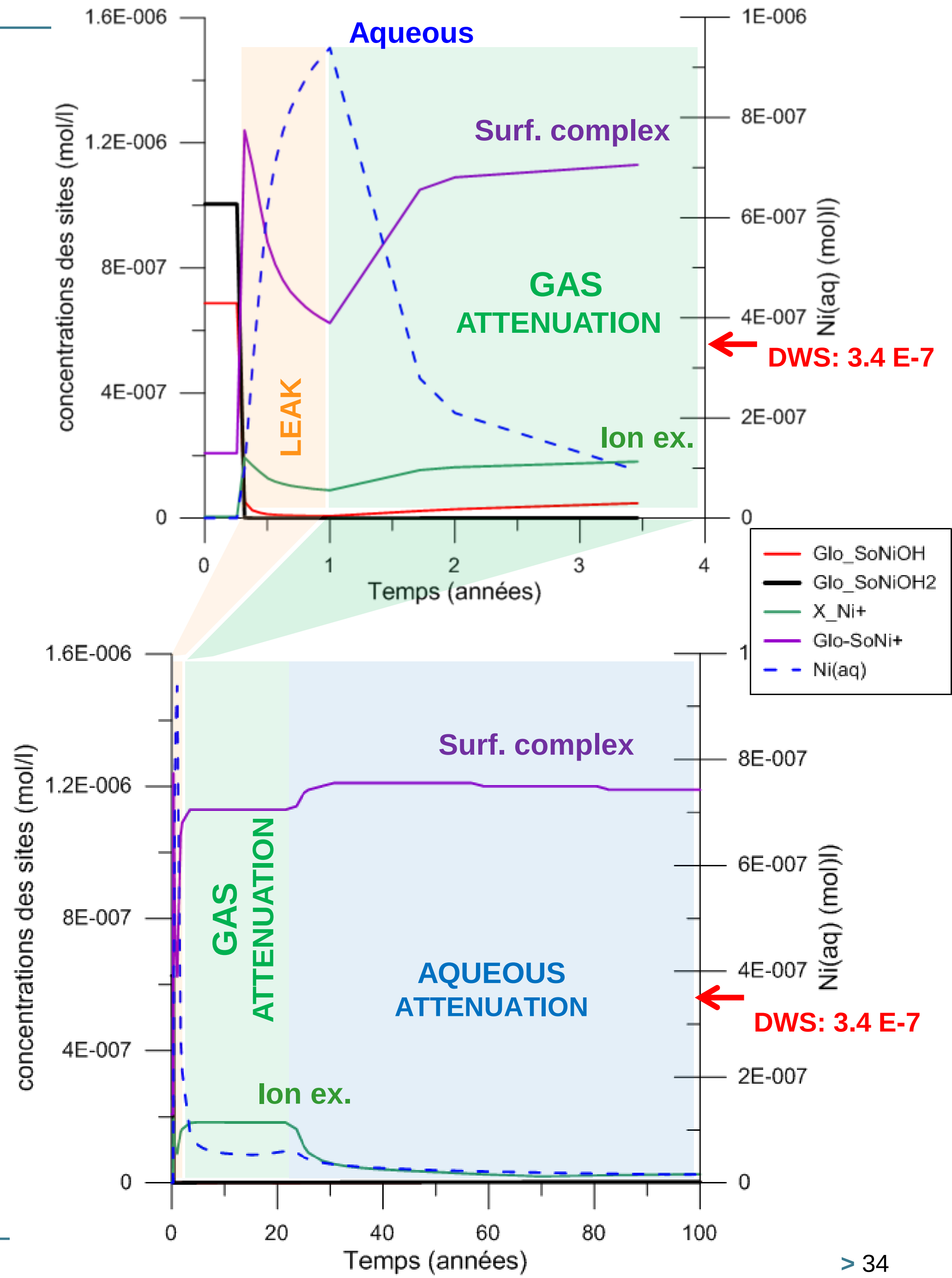
Nickel evolution with time at the leaking point

Initial distribution of Ni
- Aqueous: ε
- Exchange-Ni: +
- Surface complexes: +++

CO_2 leak
- Aqueous Ni: ++++
  - ⟶ above DWS
- Exchange-Ni: ++
- Surface complexes: +++

Attenuation of gas phase
- Aqueous Ni: +
- Exchange-Ni: +++
- Surface complexes: ++++

Attenuation of aqueous species
- Exchange-Ni: ++
- Surface complexes: ++++
- Aqueous Ni: ε



Ni evolution with time at the leaking point

> Initial distribution of Ni

- Aqueous: 0.35 nmol/l
- Ion exchange: 16 nmol/l
- Surface complexation:
  - Glco_SONi$^+$ 0.2 µmol/l
  - Glco_SONiOH 0.68 µmol/l
  - Glco_SONiOH$_2^-$ 0.62 µmol/l

> CO_2 leak

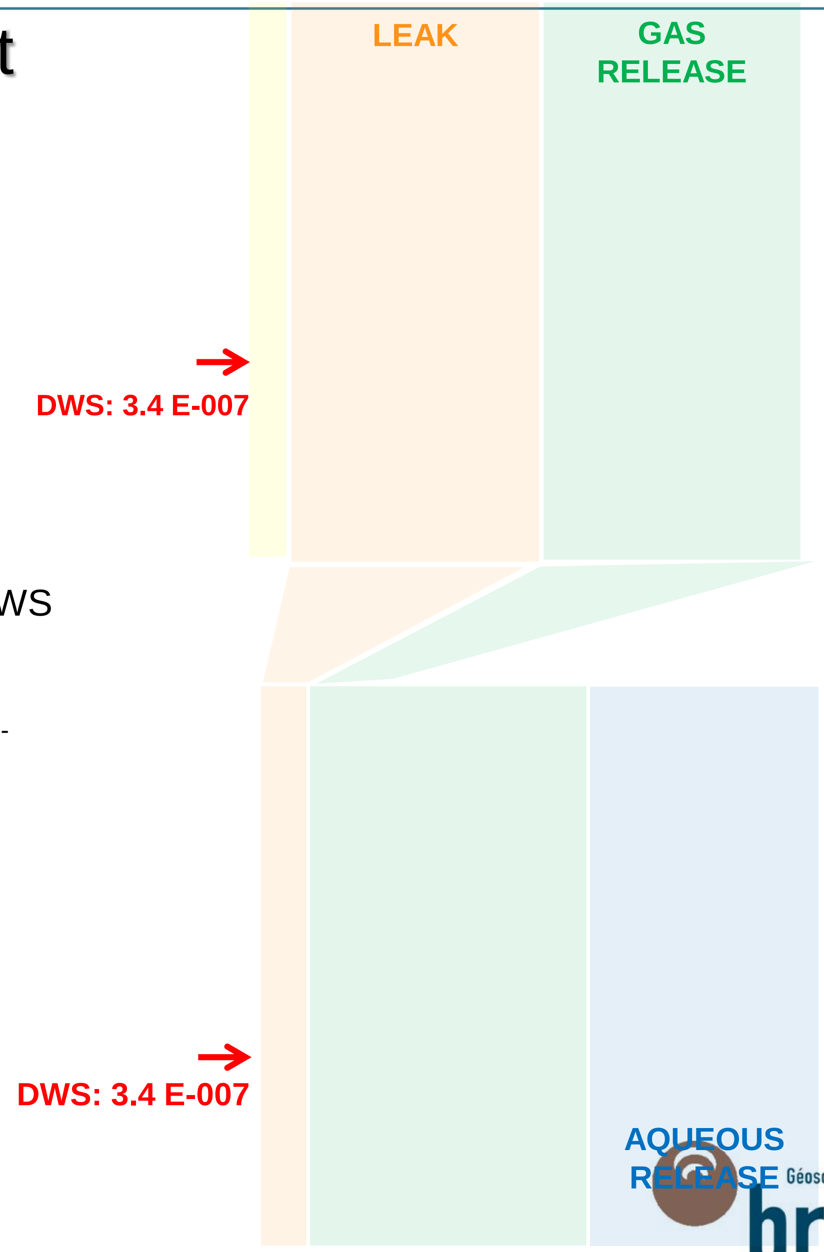
- Aqueous Ni increases above DWS
- X_Ni: exchange-Ni increases
- Glco_SONi$^+$ increases
- Glco_SONiOH, Glco_SONiOH$_2^-$ decreases

> Gas release

- Aqueous Ni decreases
- X_Ni: exchange-Ni increases
- Glco_SONi$^+$, Glco_SONiOH increases

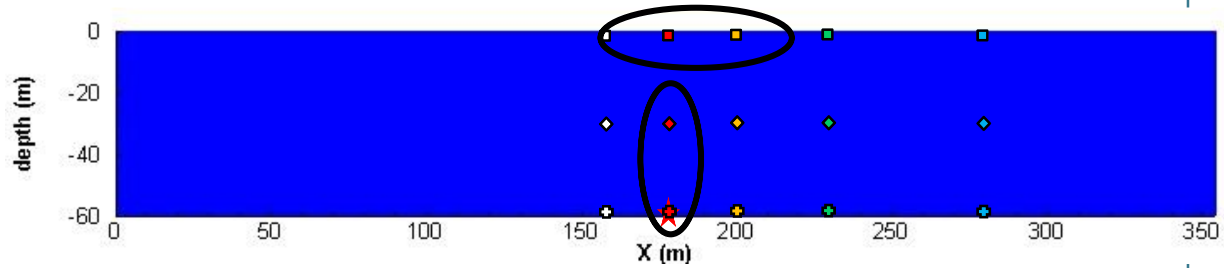
> Aqueous release

- X_Ni: exchange-Ni decreases
- Glco_SONi$^+$, Glco_SONiOH increases
- Aqueous Ni decreases



Géosciences pour une Terre durable
brgm

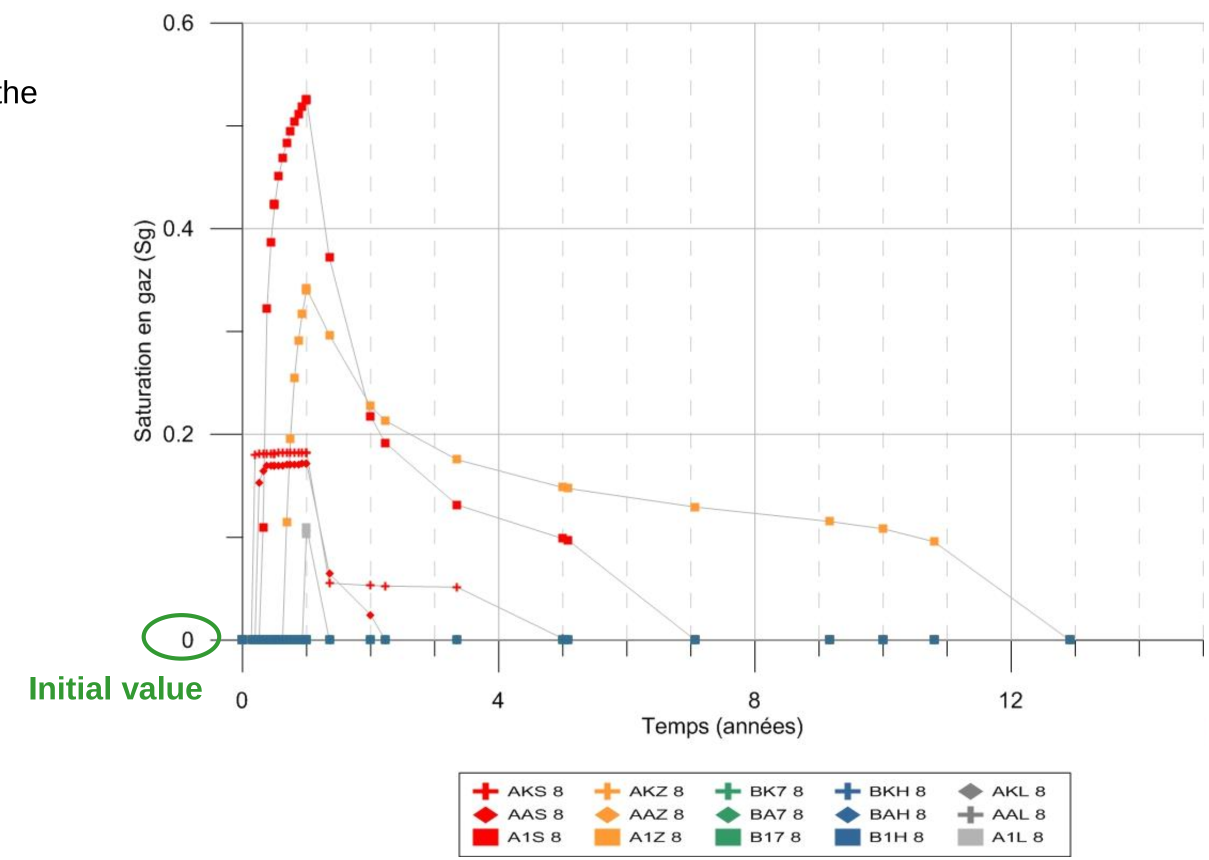
Monitoring plan



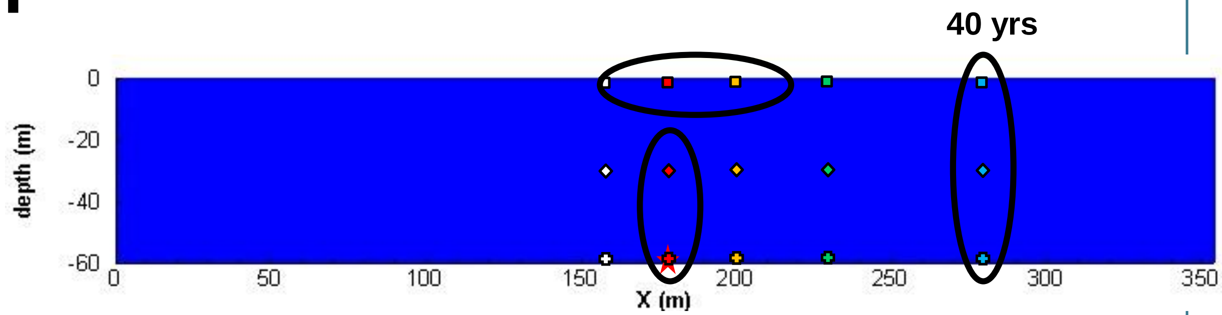
Gaz saturation

- Above the leak
- Downstream at the top of the aquifer

✓ **Natural attenuation**

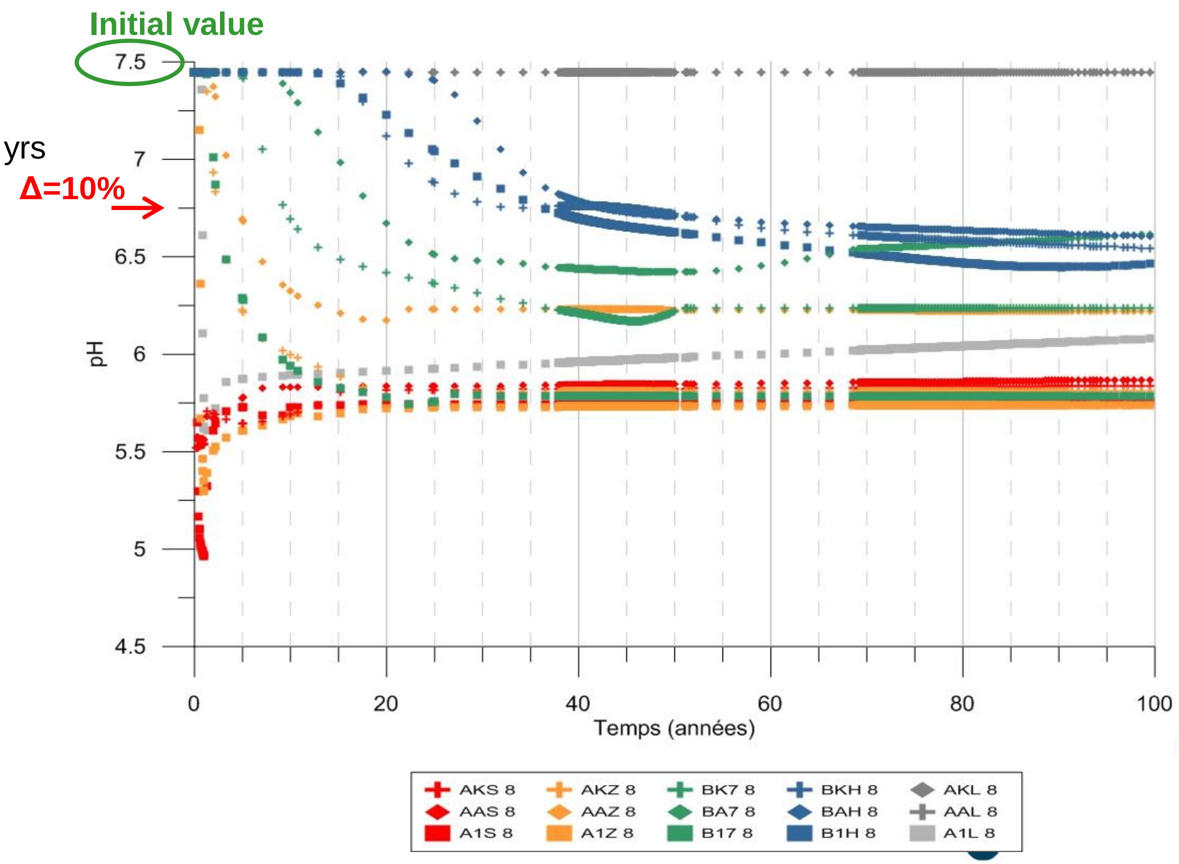


Monitoring plan

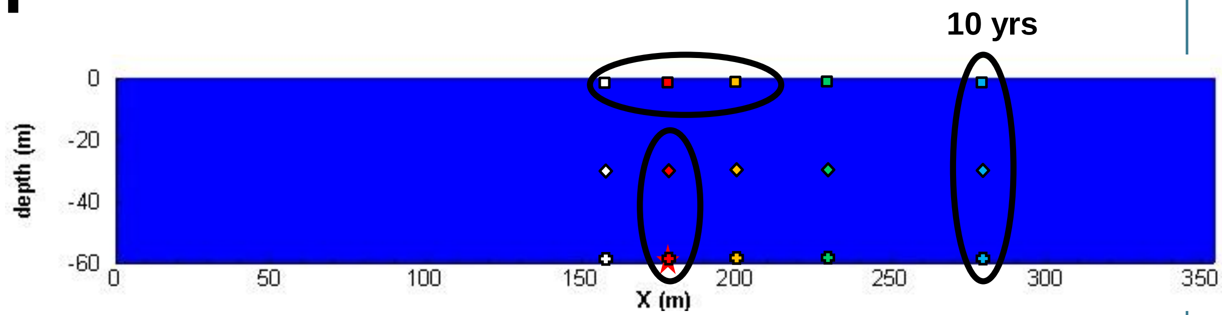


pH value

- Above the leak
- First detection at the top
- 100 m downstream after 40 yrs
- Small buffering effect

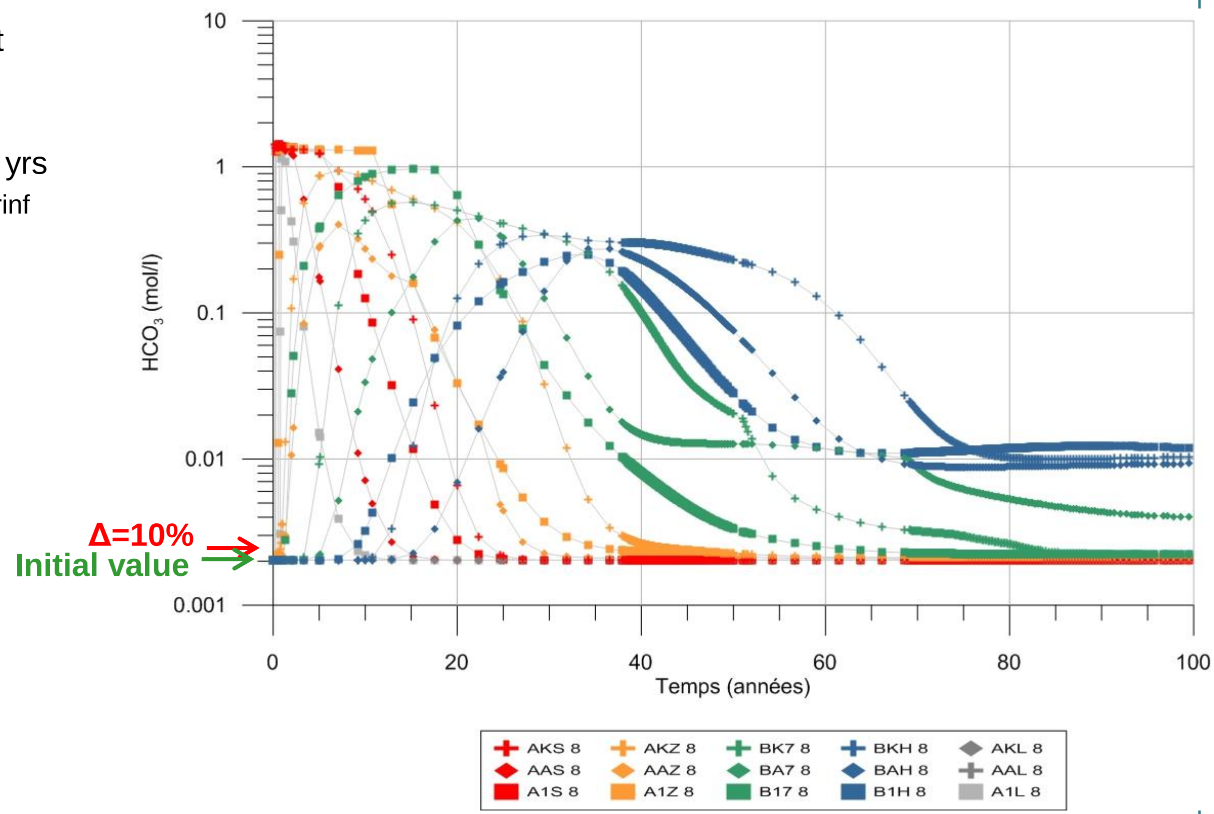


Monitoring plan

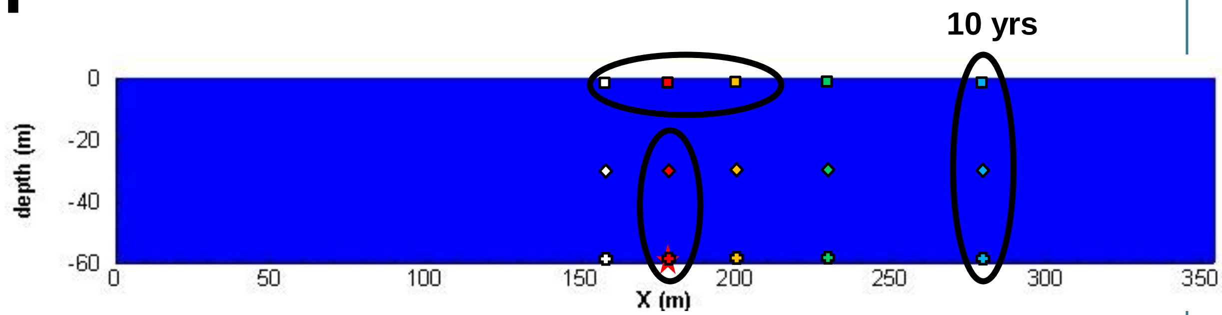


Dissolved CO_2 (eq. HCO_3)

- Above the leak
- First detection at the top but large accumulation at the bottom
- 100 m downstream after 10 yrs
  - Earlier than pH (no bufferinf effect)
- Natural attenuation



Monitoring plan



Aqueous Silica (SiO_2)

- Above the leak
- First detection at the top but large accumulation at the bottom
- 100 m downstream after 15 yrs
  - Earlier than pH (no buffering effect)
- No natural attenuation