PREDICTIVE GEOSCIENCES

FROM SCIENTIFIC CHALLENGES OF TODAY TO FIELD APPLICATIONS OF TOMORROW

Laurent ANDRE

ISTO – UMR 7327

CNRS/UNIVERSITY OF ORLÉANS/BRGM

INSTITUT CARNOT brgm

Institut des Sciences de la Terre d'Orléans ISTO

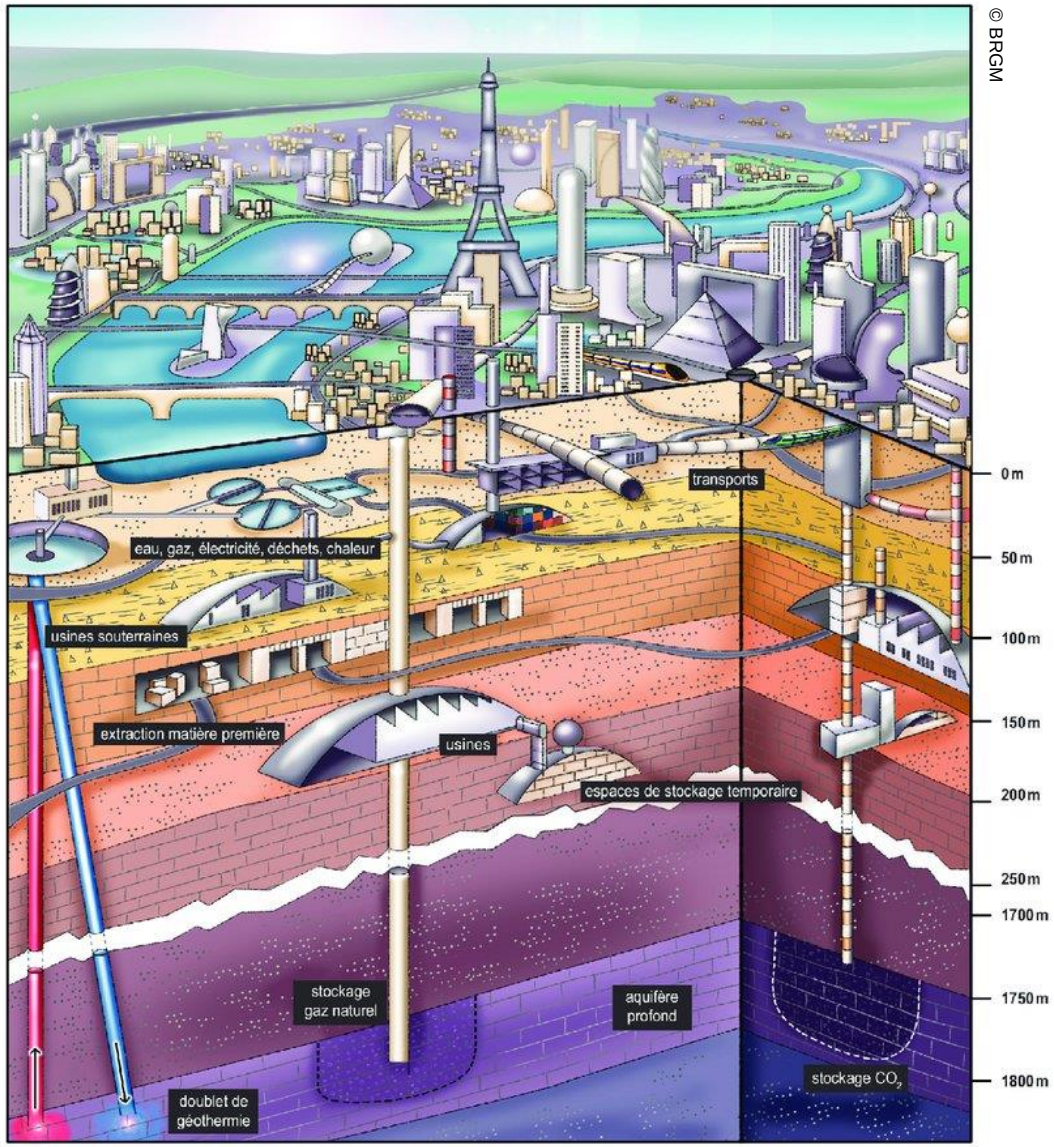
Géosciences pour une Terre durable brgm

INTRODUCTION

- Different uses of underground :
  - Networks (water, gas, electricity),
  - Geothermal energy,
  - Raw materials,
  - Transportation systems,
  - Storage facilities (CO_2, methane…)
  - Drinking water production
  - Thermalism
  - ….

- Need to better understand and predict the dynamics of sub-surface geological systems, and the interactions between the geosphere, hydrosphere, and biosphere

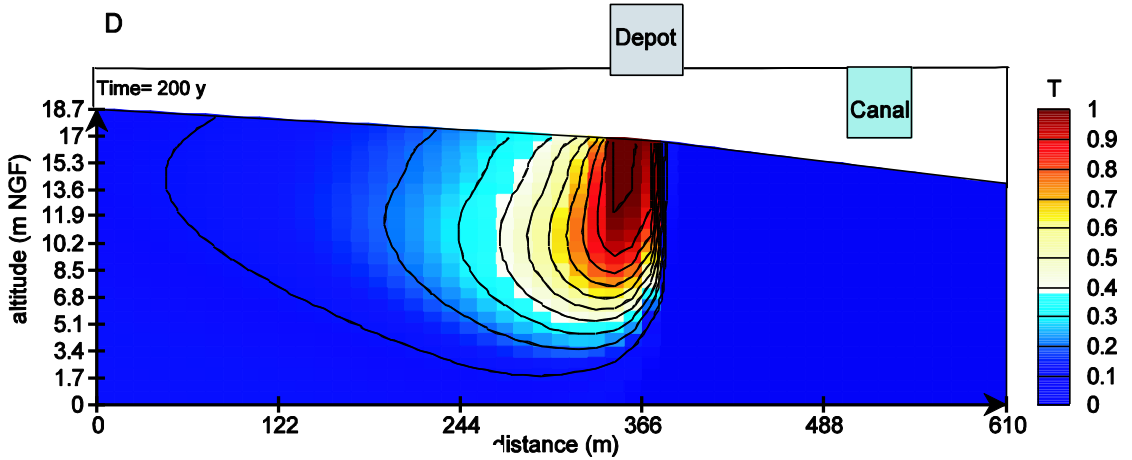
- Require rational integration of multiple and simultaneous physical, chemical and biological processes that can influence each other.

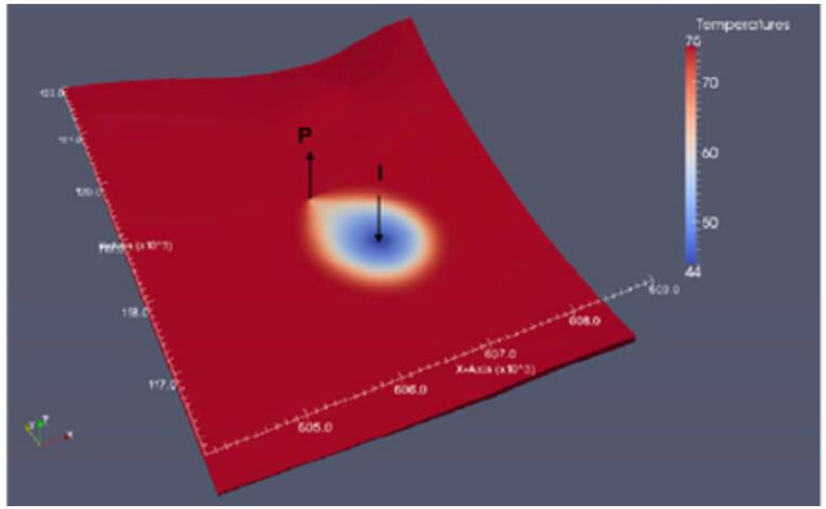


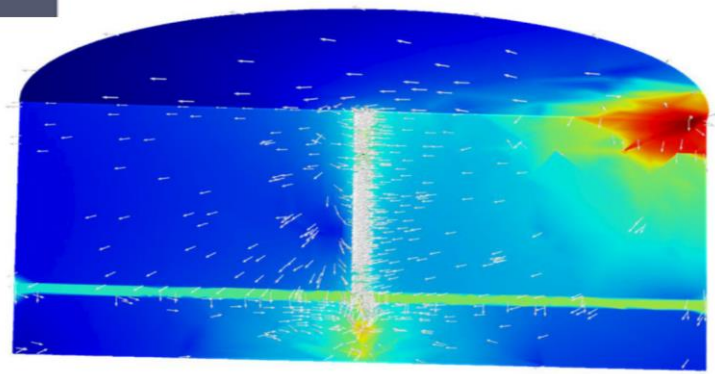
(Nehlig et al., 2016)

INTRODUCTION

- Because of the interactions of the processes, coupled modeling approaches are needed
- Reactive transport modelling are transfer models in wetting and non-wetting phases (water, gas, oil) coupled with chemical reactive models between the fluid and the organic/inorganic components and minerals from the basement
- These models allowed remarkable progresses on a broad field of studies:
  - pollutant transfers in soils and aquifers,
  - basement exploitation for storages of gas and radioactive wastes,
  - exploration and exploitation of raw materials and geothermal energy.







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INTRODUCTION

- The development of these numerical tools gradually emerged as the main way to achieve the relationship between the knowledge of fundamental processes taken individually, and the predictions carried out in environmental sciences, which are necessary for a rational management of the soil and subsoil resources.

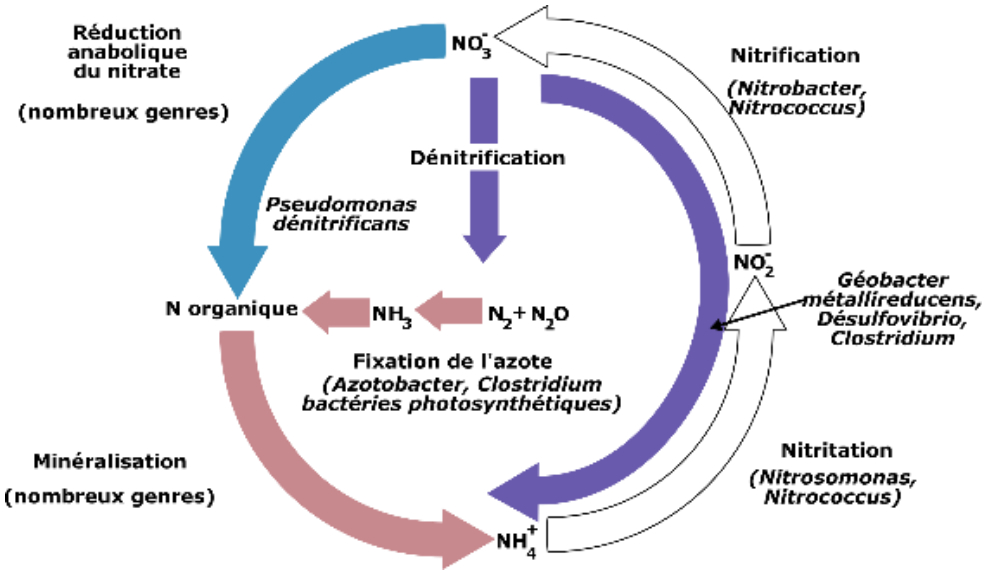
- Despite many achievements, there are still many scientific challenges associated with these numerical approaches
  - Some mechanisms of transfer and reactivity are not taken into account by the existing digital codes.
  - Conversely, some mechanisms managed by the codes may not be considered due to the lack of experimental data.

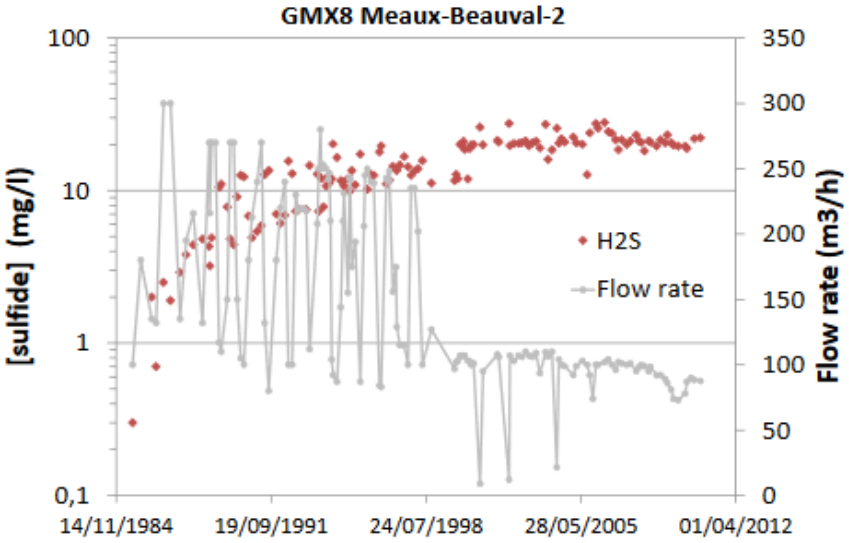
Overview of the presentation

- **Biochemical reactions**
  - An experimental and modelling coupled approach – Application to denitrification
- **Multiphasic systems**
  - The necessity to use coupled approaches – Application to CO_2 storage in deep geological reservoirs
- **Conclusions and Perspectives**

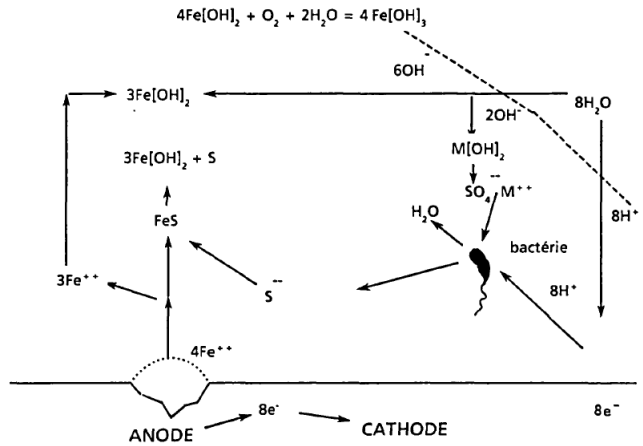
Context of biochemical reactions

- Micro-organisms are everywhere !
- Role in surface and subsurface ecosystems : cycles of nitrogen, carbon, sulphur,
- Role in depollution of soils, peatlands…
- Role in deep aquifers : H_2S, CO_2
- Role in deep oil and gas reservoirs : CH_4
- Role of microorganisms in surface installations : scaling issues, corrosion…
- ….





(Castillo and Ignatiadis, 2011)



(Le Dinh Bao, 1990)

Modelling of the microorganisms processes

- The ***Michaelis-Menten's equation*** (1913)
  - Enzymatic reactions (sucrose -> fructose + glucose)
  - Reaction rate function of reactives/products/enzyme concentrations

$$v = C.\emptyset.\frac{[S]}{k + [S]}$$

- The ***empirical approach of Monod*** (1949)
  - Bacterial growth
  - Reaction rate function of substrate and biomass concentrations

$$v = k.[X].\frac{[D]}{K_D + [D]}.\frac{[A]}{K_A + [A]}$$

=> Useful to describe the relation between bacterial growth and substrate concentration in batch systems, but this modelling comprises however some restrictions (Not correctly predict the reaction rates when substrate concentrations are very weak ⇒ approach devoted to describe processes which are far from thermodynamic equilibrium).

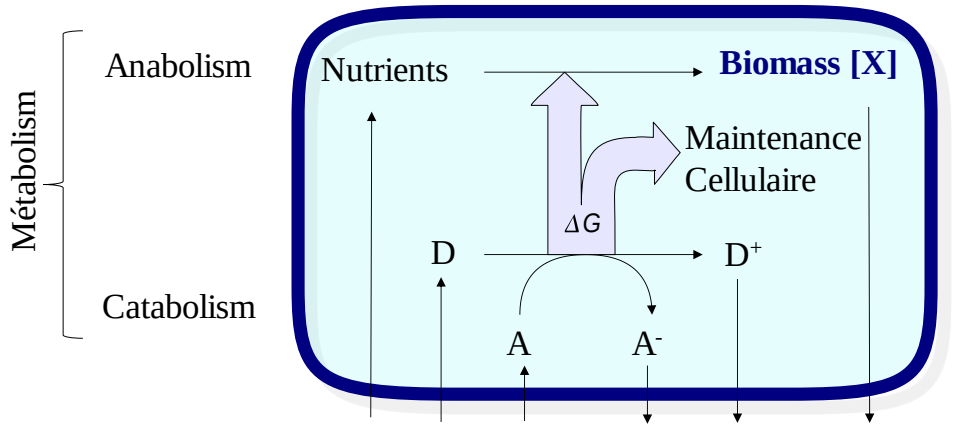
- The ***coupling between kinetic and thermodynamic bacterial growth (1990-2000)***
  - Hoh & Cord-Ruwisch, 1996
  - Fennel & Gossett, 1998
  - Noguera *et al*., 1998
  - Kleerebezem & Stams, 2000

=> Nevertheless, approaches generally established to describe specific physiological systems and they are not easily transposable with broader studies.

Theoretical approach for modelling microorganism activity

For their growth, micro-organisms need energy that they take from the chemical energy available in their environment.

Jin and Bethke (2002-2007) proposed a comprehensive and global approach coupling micro-organism respiration and redox processes (TEAPs)



$$\sum_D \nu_D D + \sum_A \nu_A A + m\,ADP + m\,P_i \overset{\nu}{\longleftrightarrow} \sum_{D^+} \nu_{D^+} D^+ + \sum_{A^-} \nu_{A^-} A^- + m\,ATP$$

Respiration kinetics (mol L^{-1} s^{-1})

Kinetic Constant (mol g^{-1} s^{-1})

Kinetic factors dependent on concentrations of electron donor/acceptor

$$V = k.[X].F_D.F_A.F_T$$

Biomass concentration (g L^{-1})

Thermodynamic Potential of the overall reaction

Theoretical approach for modelling microorganism activity

Kinetic factors dependent on concentrations of electron donor/acceptor

$$F_D = \frac{\prod_D [D]^{\beta_D}}{\prod_D [D]^{\beta_D} + K_D \prod_{D^+} [D^+]^{\beta_{D^+}}}$$

$$F_A = \frac{\prod_A [A]^{\beta_A}}{\prod_A [A]^{\beta_A} + K_A \prod_{A^-} [A^-]^{\beta_{A^-}}}$$

- F_D, F_A : kinetic factors allowing to consider the effects of the concentration of dissolved chemical species involved in redox reactions
- β_D, β_A, β_{D+}, β_{A-} : exponents of reactive and product concentrations
- K_D, K_A : half-saturation constants for electron donor D and acceptor A

Biomass concentration (g L^{-1})

$$\frac{d[X]}{dt} = Yv - D[X]$$

- *Y* growth field (grams of biomass produced per mole of reaction)
- *D* decay factor (s^{-1})

Theoretical approach for modelling microorganism activity

Originality of the approach: the dependence on the thermodynamic factor (F_T) which is function of redox reaction enthalpy

$$F_T = 1 - \exp\left(\frac{\Delta G_{redox} + m\,\Delta G_P}{\chi RT}\right)$$

$$\Delta G_{redox} = \Delta G^0_{redox} + RT\,ln\left(\frac{\prod_{D^+} a_{D^+}^{\nu_{D^+}} \prod_{A^-} a_{A^-}^{\nu_{A^-}}}{\prod_{D} a_{D}^{\nu_{D}} \prod_{A} a_{A}^{\nu_{A}}}\right)$$

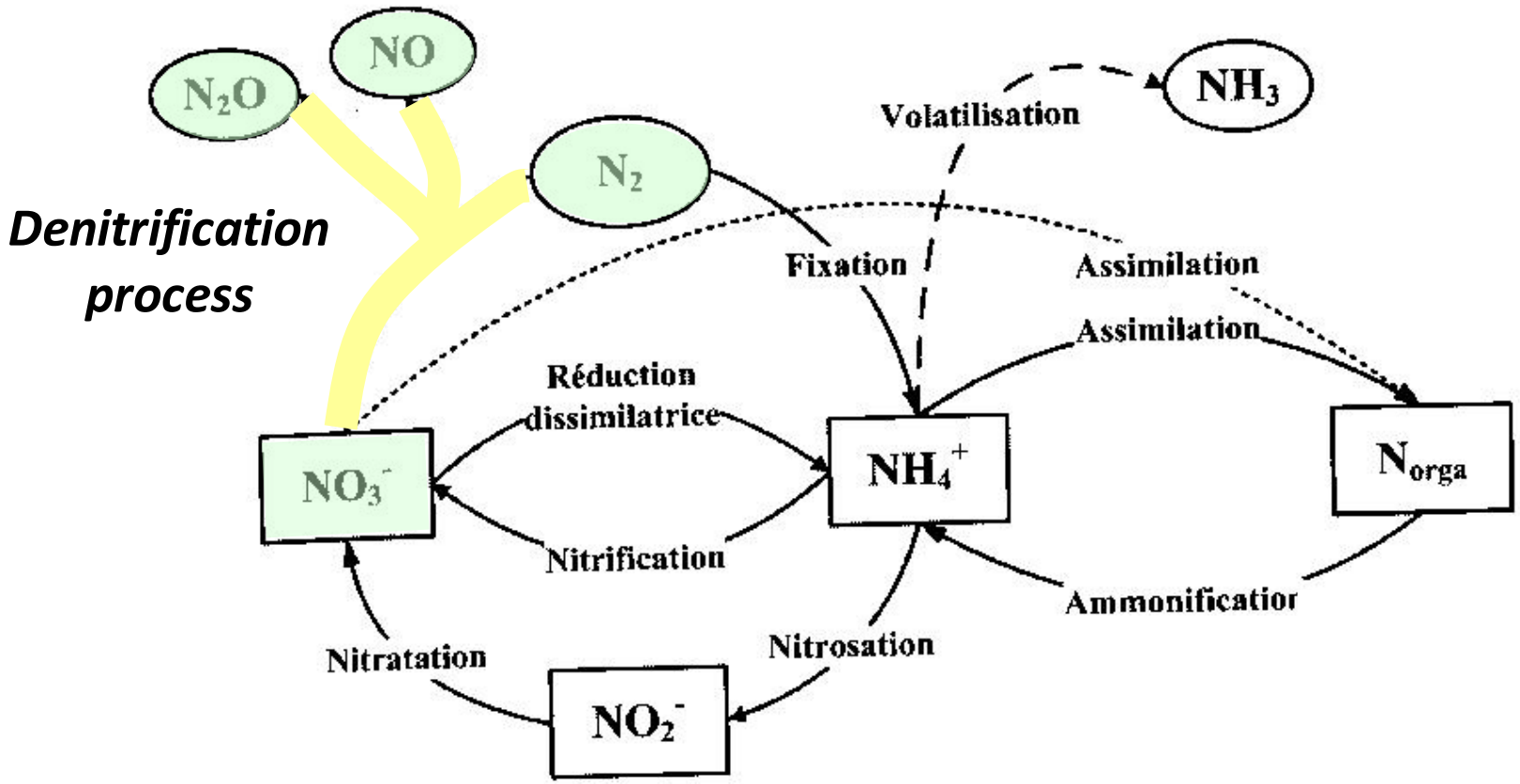
χ : Mean stoichiometric number
m : Number of synthesized moles of ATP

Reactions	ΔG^0_r (kJ mol^{-1})
$5\ Fe^0_{(s)} + 2\ NO_3^- + 12\ H^+ = N_{2(g)} + 5\ Fe^{2+} + 6\ H_2O$	-804.0
$5\ H_{2(aq)} + 2\ NO_3^- + 2\ H^+ = N_{2(g)} + 6\ H_2O$	-618.3
$5\ CH_3COO^- + 8\ NO_3^- + 3\ H^+ = 4\ N_{2(g)} + 10\ HCO_3^- + 4\ H_2O$	-505.7
$5\ FeS_{2(s)} + 14\ NO_3^- + 4\ H^+ = 7\ N_{2(g)} + 10\ SO_4^{2-} + 5\ Fe^{2+} + 2\ H_2O$	-428.7
$5\ Fe^{2+} + NO_3^- + 7\ H_2O = 0.5\ N_{2(g)} + 5\ FeOOH_{(s)goethite} + 9\ H^+$	-268.5
$5\ Fe^{2+} + NO_3^- + 7\ H_2O = 0.5\ N_{2(g)} + 5\ FeOOH_{(s)amorphe} + 9\ H^+$	-139.5

	$\Delta E^{\circ\prime}$ (V)[a]	χ[b]	m[b]
Oxygen respiration (*Paracoccus denitrificans*[c]) $H_2 + \frac{1}{2} O_2 \rightleftarrows H_2O$	1.23	4	2
Denitrification (*Paracoccus denitrificans*) $H_2 + \frac{2}{5} NO_3^- + \frac{2}{5} H^+ \rightleftarrows \frac{1}{5} N_2 + \frac{6}{5} H_2O$	1.2	2	2/3
Sulfate reduction (*Desulfovibrio vulgaris*) $H_2 + \frac{1}{4} H^+ + \frac{1}{4} SO_4^{2-} \rightleftarrows \frac{1}{4} HS^- + H_2O$	0.193	2	1/3
Methanogenesis $H_2 + \frac{1}{4} H^+ + \frac{1}{4} HCO_3^- \rightleftarrows \frac{1}{4} CH_4 + \frac{3}{4} H_2O$	0.17	2	2/9

Application to the modelling of denitrification processes

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$



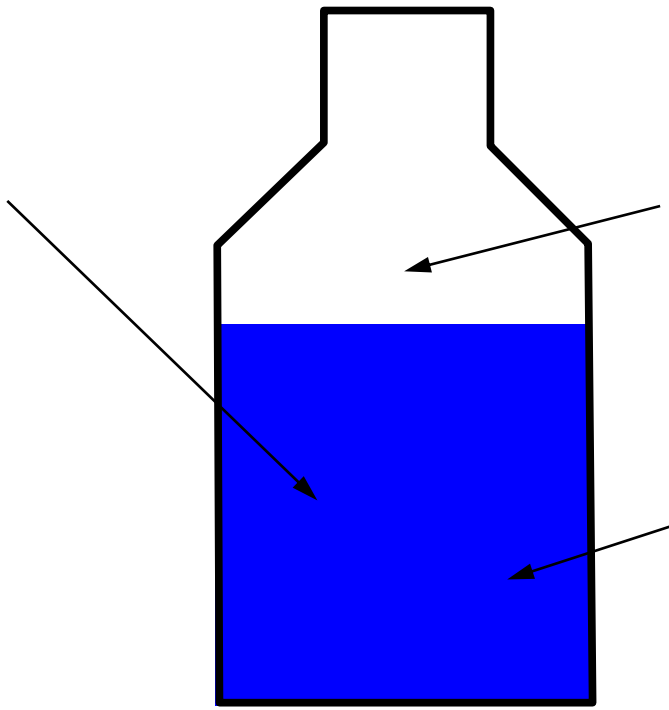
Lab experiments in closed systems (batch)

Groundwater samples (France).
Composition:

pH	5.6
Cl^-	0.79 mM
Na^+	1.64 mM
Ca^{2+}	0.44 mM
Mg^{2+}	0.38 mM
SO_4^{2-}	0.32 mM
K^+	0.059 mM
Fe	0.082 mM

+ inoculums

(Pauwels et al., 2000)



CO_2 atmosphere with 6.7 vol% of acetylene to prevent N_2O to N_2 reduction reaction

CH_3COONa 50 mg/l
NO_3Na 50 mg/l

- *Experiments performed at 14°C during 2 months.*
- *Measurements of NO_3, NO_2 , N_2O, Acetate concentrations, biomass, pH*

Application to the modelling of denitrification processes

Reactions modelled : Catabolism + anabolism

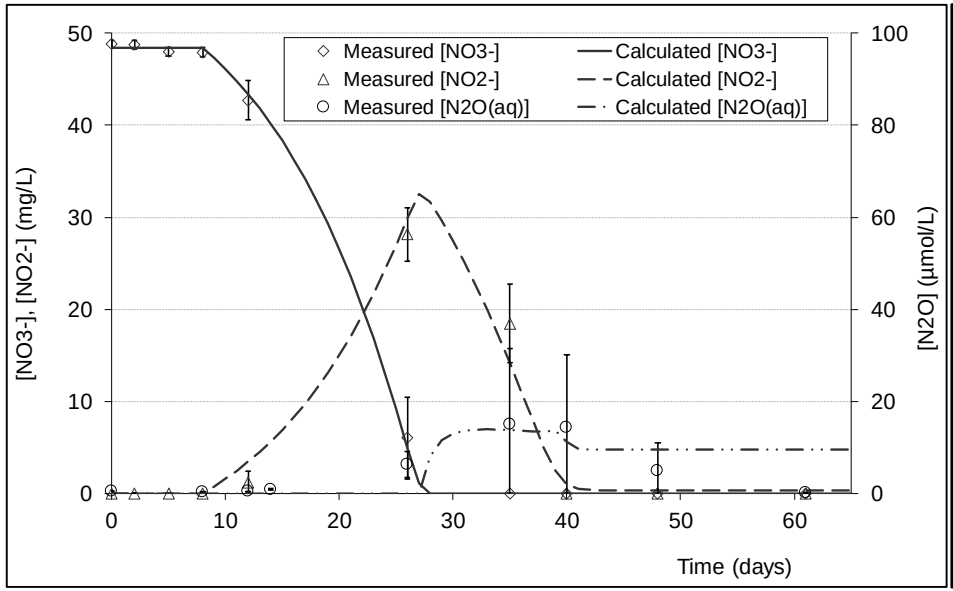
$$NO_3^- + {}^{27}\!/_{56}\, CH_3COO^- + {}^{31}\!/_{56}\, H^+ \rightarrow {}^{13}\!/_{14}\, NO_2^- + {}^{1}\!/_{14}\, C_5H_7O_2N + {}^{17}\!/_{28}\, CO_{2(aq)} + {}^{3}\!/_{4}\, H_2O$$

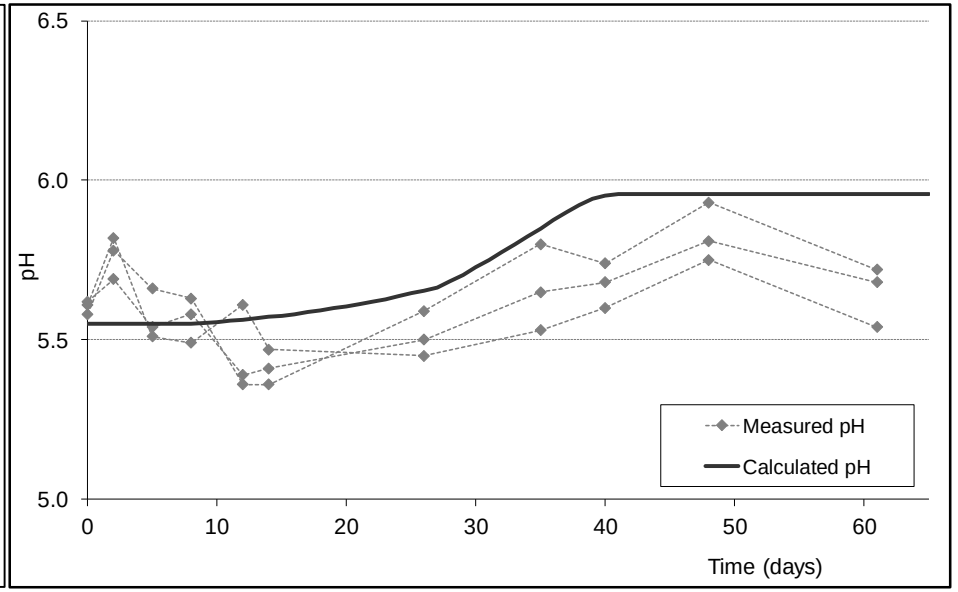
$$NO_2^- + {}^{11}\!/_{20}\, CH_3COO^- + {}^{13}\!/_{10}\, H^+ \rightarrow {}^{9}\!/_{20}\, N_2O + {}^{1}\!/_{10}\, C_5H_7O_2N + {}^{3}\!/_{5}\, CO_{2(aq)} + {}^{5}\!/_{4}\, H_2O$$

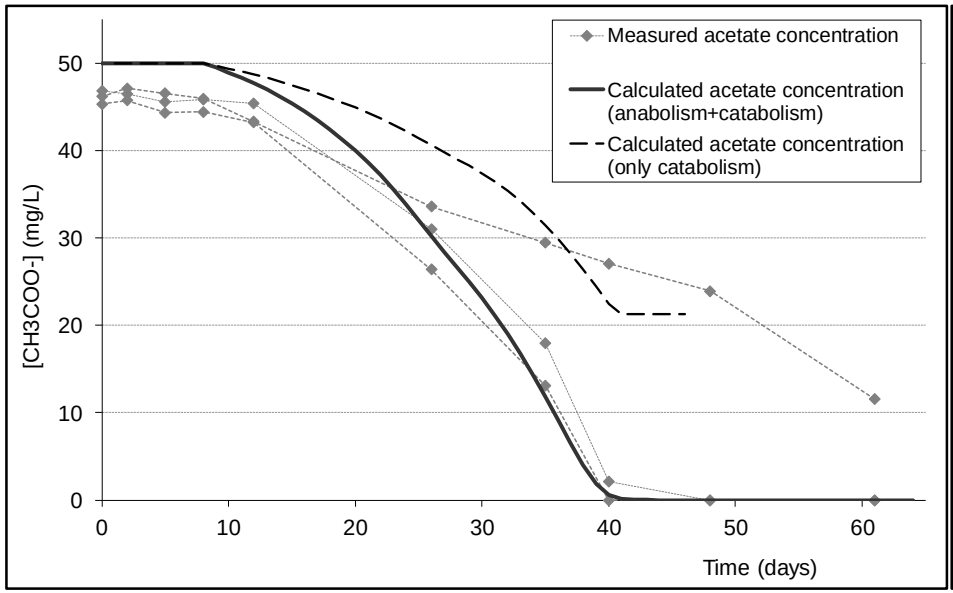
$$N_2O + {}^{51}\!/_{112}\, CH_3COO^- + {}^{51}\!/_{112}\, H^+ \rightarrow {}^{27}\!/_{28}\, N_2 + {}^{1}\!/_{14}\, C_5H_7O_2N + {}^{31}\!/_{56}\, CO_{2(aq)} + {}^{37}\!/_{56}\, H_2O$$

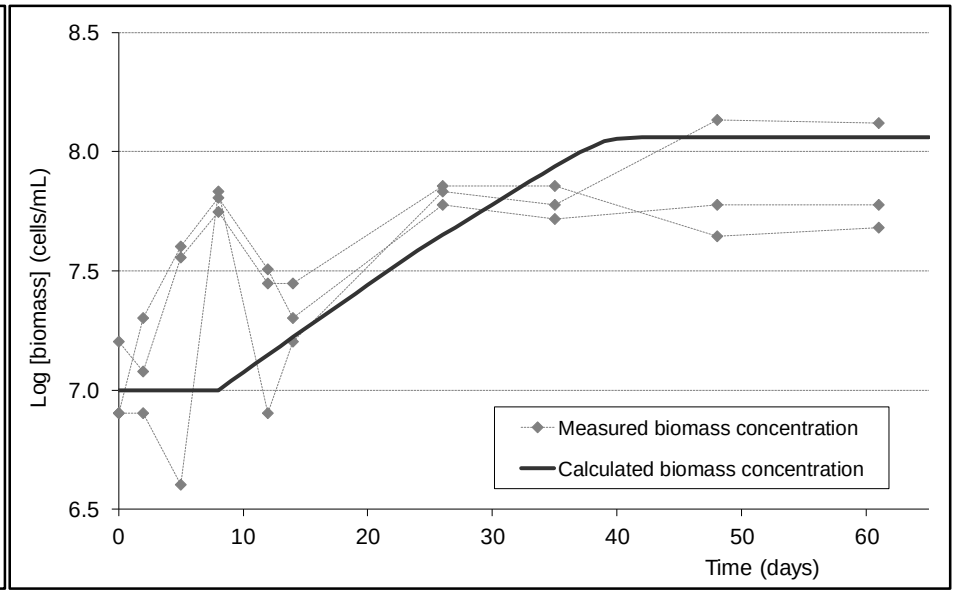
- Calculations done with Phreeqc code (Parkhurst and appelo, 2013)
- Kinetic approach proposed Jin & Bethke, 2007
- Main Kinetic Parameters from litterature
  - $K_{acetate}$, $K_{nitrate}$, $K_{nitrite}$, Y_1, Y_2 from Clément et al. (1997)
  - m, χ from Jin & Bethke (2007)
  - ΔG_P from White (1995)
- Only kinetic constants are adjusted

Chemical variations according to time





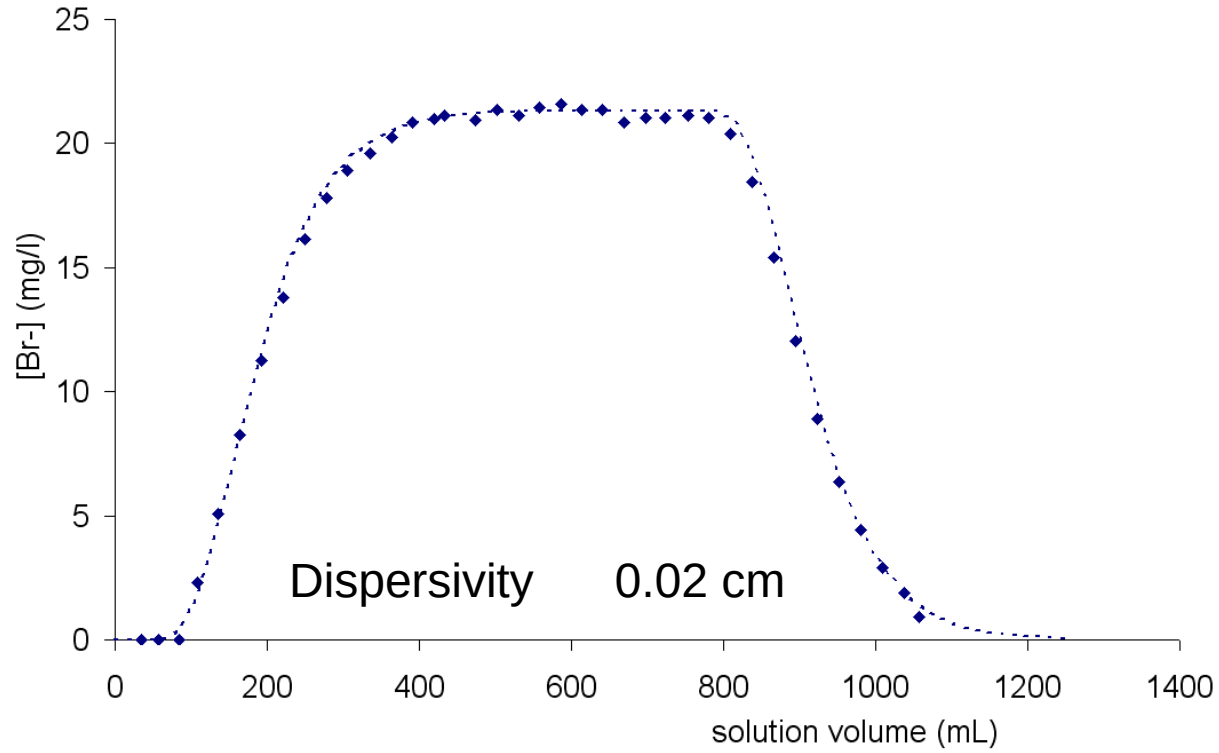




(André et al., 2009)

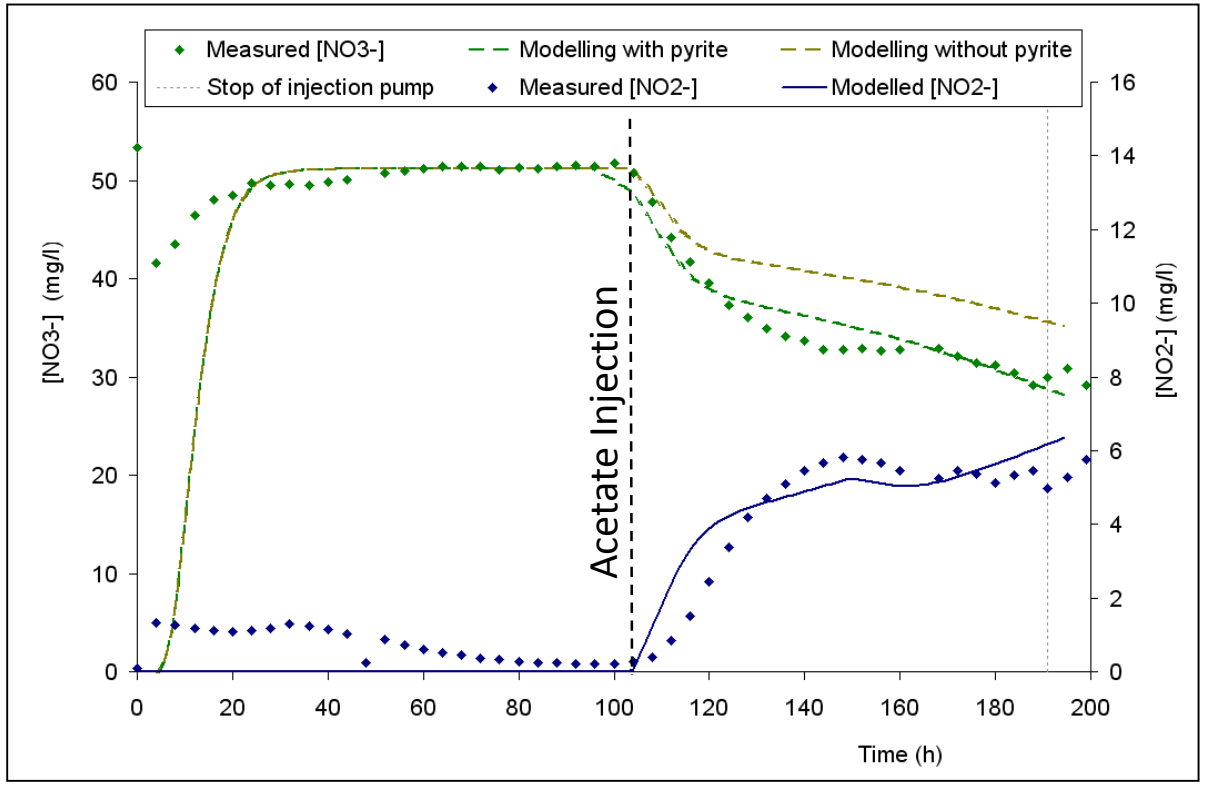
Experiments in 1D-flow through column

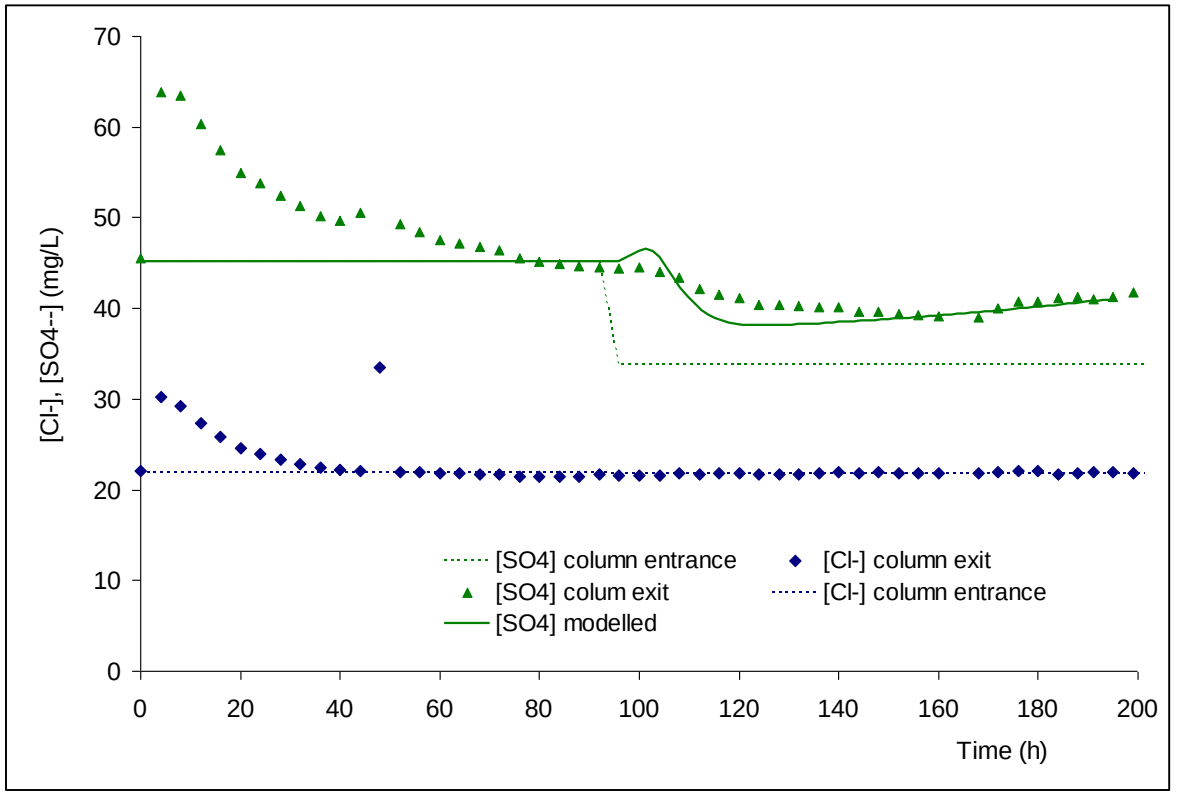
- Percolation of a nitrated solution through a schist-bearing column
- Characterisation of the hydraulic properties of the column
- Analysis of the outlet solution to follow the denitrification process
- What about the upscaling from batch systems to 1D system ?



Chemical variations at the column outlet

(André et al., 2009)





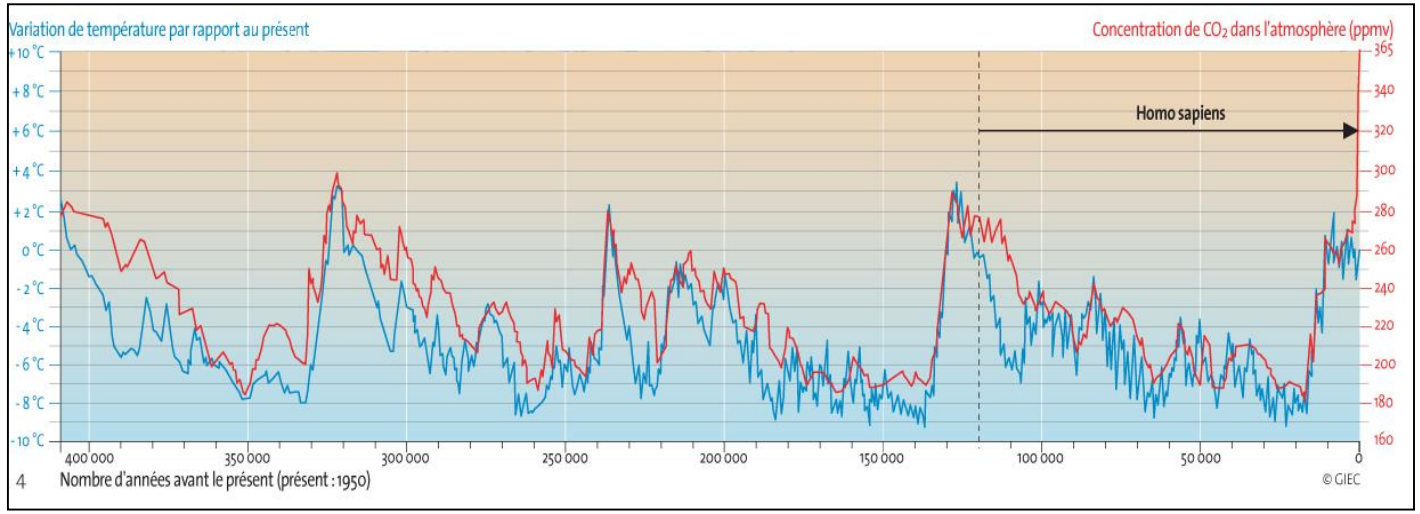
- Denitrification processes is a kinetic process controlled by microorganisms
- The model reproduces experimental data (NO_2^-, N_2O, N_2, bacterial growth…) using the same kinetic rates than in batch system
- Encouraging results with respect to the upscaling (from lab to field)

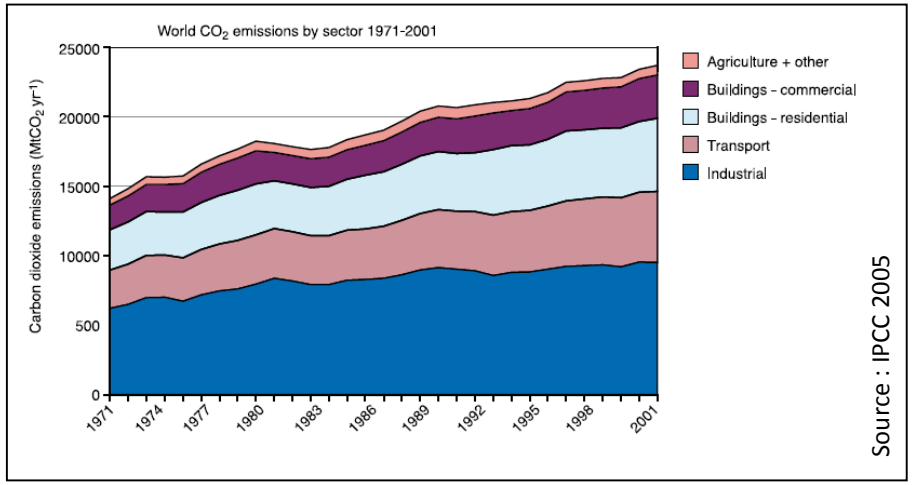
Overview of the presentation

- **Biochemical reactions**
  - An experimental and modelling coupled approach – Application to denitrification
- **Multiphasic systems**
  - The necessity to use coupled approaches – Application to CO_2 storage in deep geological reservoirs
- **Conclusions and Perspectives**

CO_2 storage in deep reservoirs : the context

- To save energy (Sobriety and energy efficiency)
- To develop the use of sustainable energy
- To capture CO_2 from industries et to store it (CCS)
  - in ocean – a controversed way
  - new concepts (ex-situ carbonatation, …)
  - in deep geological reservoirs – preferred option
- …..





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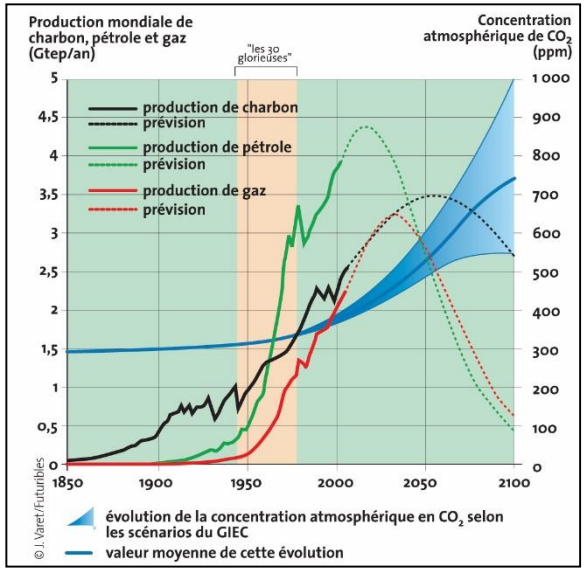
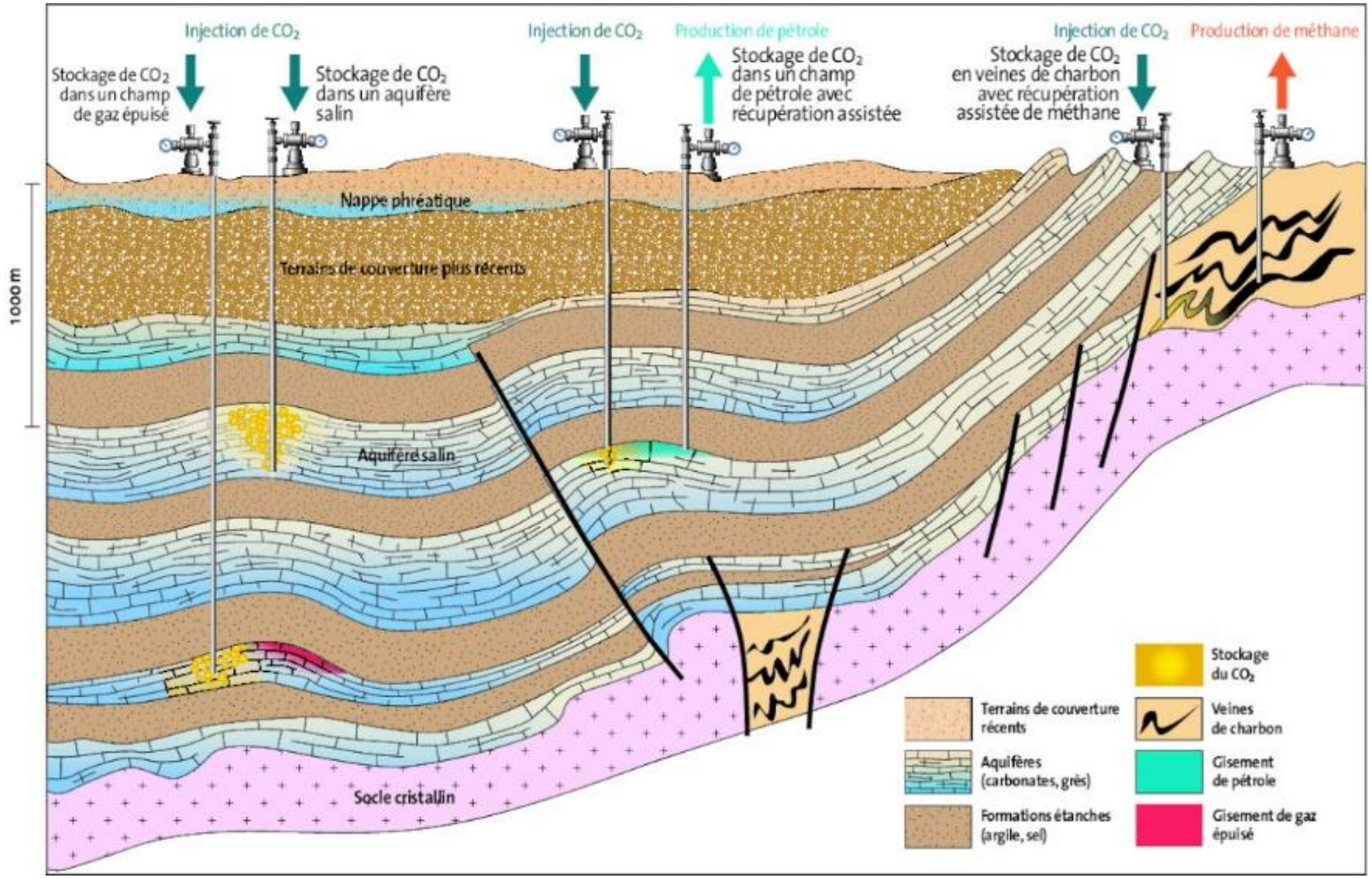


CO_2 storage in deep reservoirs : the context



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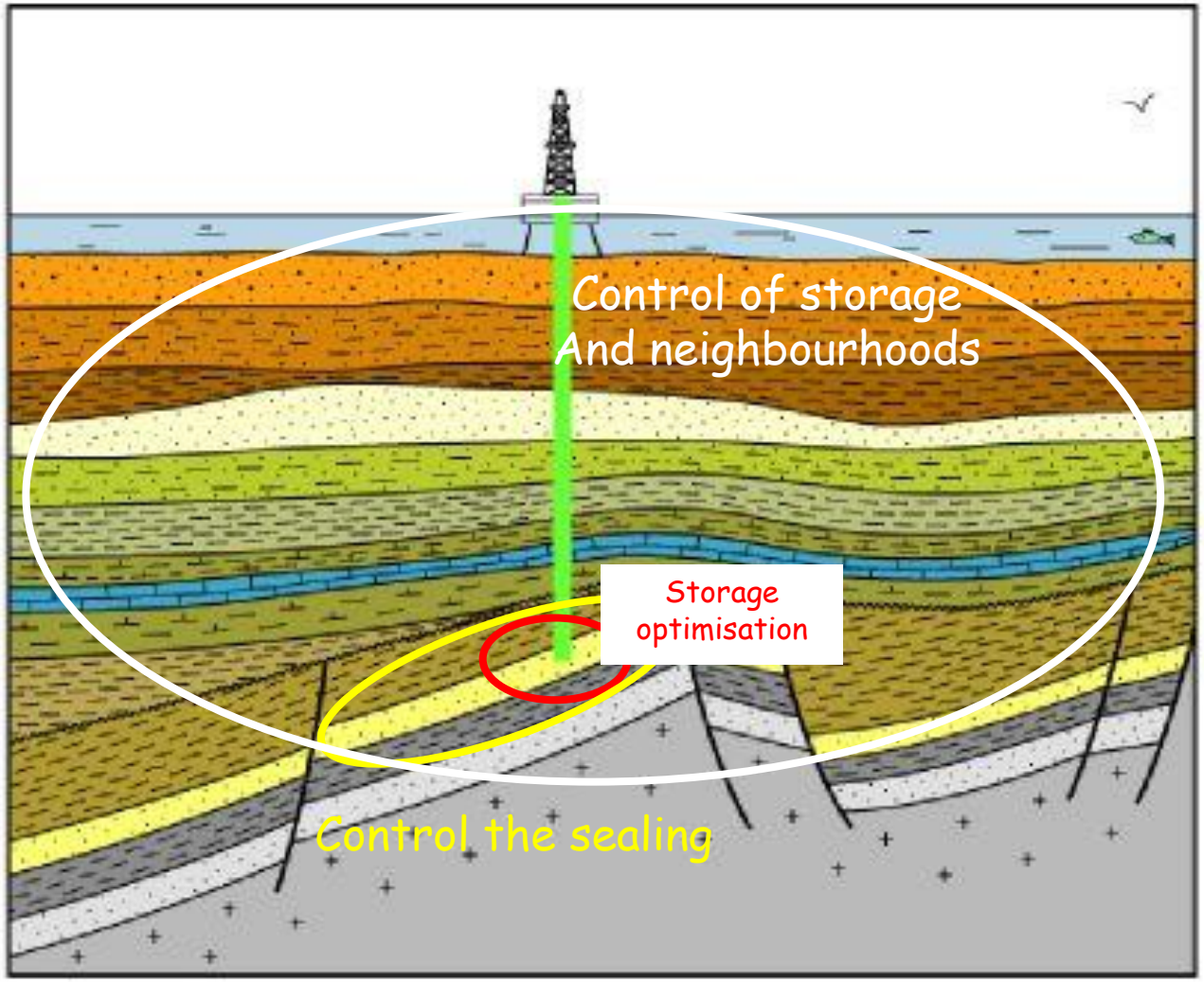
Main technical issues of underground storage : Efficiency and Security during several centuries



- Selection of relevant sites
- Understanding of physical, thermal, chemical, mechanical processes
- Coupled predictive Modelling
- Monitoring of the sites
- Risk assessment and remediation

CO_2 storage in deep reservoirs : the main challenges

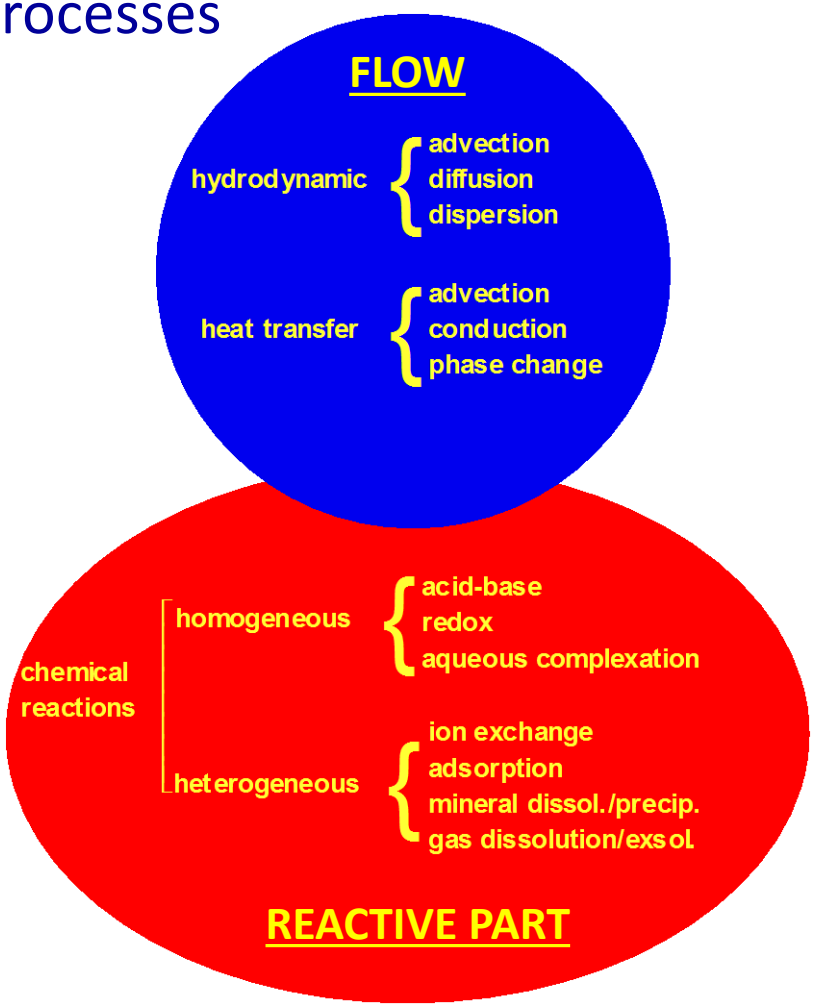
- **Hydraulic**: pressure management in the reservoir, flow rates, well characteristics, fracturing risks…
- **Thermal**: impact of low-temperature injections, thermal fracturing …
- **Mechanical**: permeability changes due to fluid injection affecting the effective stress
- **Chemical**: Impact of temperature and pressure variations on the mineral solubility, precipitation of secondary minerals and impact on permeability/porosity changes,

Non-linearity of the key processes involves the necessity to use adequate numerical tools associated to relevant thermodynamic databases to deal with reactive transport modelling

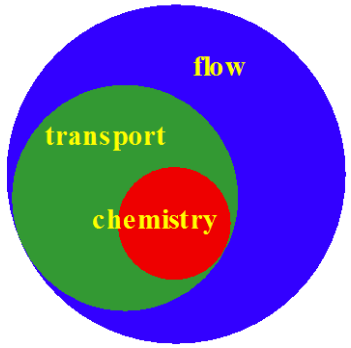
Some examples of the main outcomes of "Reactive Transport Modelling" applied to CO_2 injection in deep aquifers

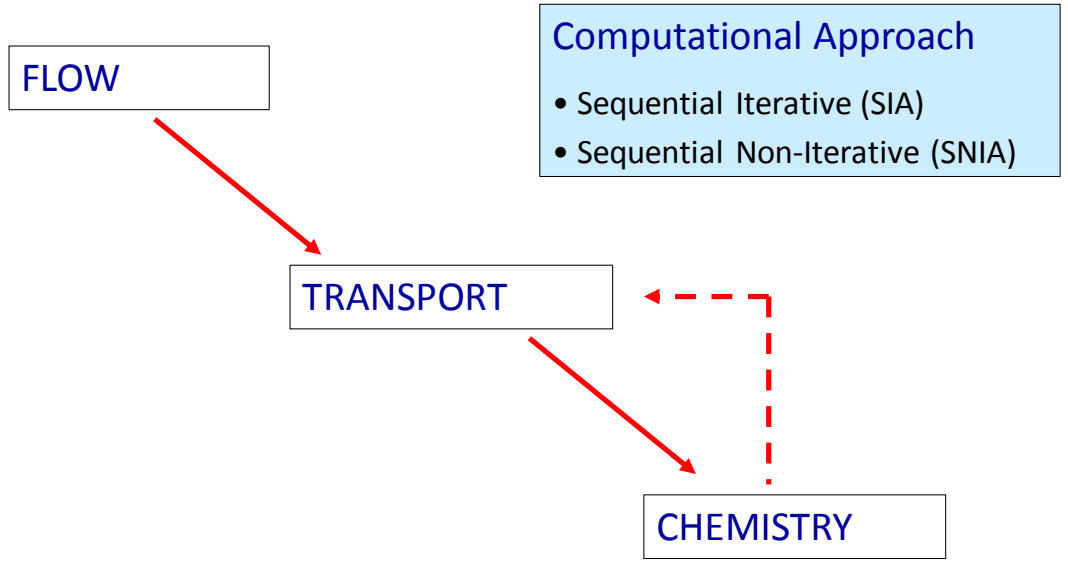
Reactive Transport Coupled-Code capabilities

Processes



- Reactions between gas - aqueous - solid phases, equilibrium or kinetics
- General database for minerals, aqueous and gaseous species
- Porosity and permeability change





Modelling of flow and transport processes in the reservoir

- Main equation of flow
  - Darcy's Law : in 1D $F = -k \frac{\rho}{\mu} \frac{\Delta P}{\Delta x}$ or in 3D $\mathbf{F} = -k \frac{\rho}{\mu} (\nabla P - \rho \mathbf{g})$

- Main equation of mass transport
  - Advective mass flux for fluid mixtures: water, solutes (NaCl, CO_2 …) and non-condensible gases (NCGs)
  - Diffusion $\mathbf{f}_\beta^\kappa = -\phi \tau_0 \tau_\beta \rho_\beta d_\beta^\kappa \nabla X_\beta^\kappa$
  - Hydrodynamic dispersion

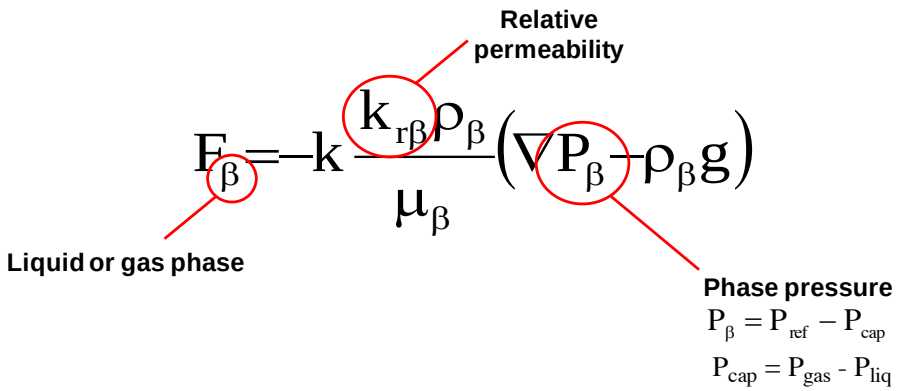
- Equations for multiphasic systems

Relative permeability functions :

- Linear functions,
- Corey curves,
- Grant's curves,
- Fatt and Klikoff functions,
- Van Genuchten-Mualen model,
- Verma et al. functions

Capillary pressure functions *:*

- Linear function,
- Pickens et al. function,
- TRUST capillary pressure,
- Leverett's function,
- Van Genuchten function,
- No capillary pressure



Mass Balance and Energy Balance Equations

change in fluid mass in volume V = net fluid inflow across surface of V + net gain of fluid from sinks and sources

$$\frac{d}{dt}\int_{V_n} M^\kappa \, dV_n = \int_{\Gamma_n} \mathbf{F}^\kappa \bullet \mathbf{n} \, d\Gamma_n + \int_{V_n} q^\kappa dV_n$$

Forms of Mass accumulation term

single phase, single component	$M = \phi \rho$
single phase, multi-component	$M^\kappa = \phi \rho X^\kappa$
multi-phase, multi-component	$M^\kappa = \phi \sum_\beta S_\beta \rho_\beta X_\beta^\kappa$

change in internal energy in volume V = net transfer of energy by fluid flow + mechanical work done to volume V + net heat transfer by conduction + net energy gain from sinks and sources

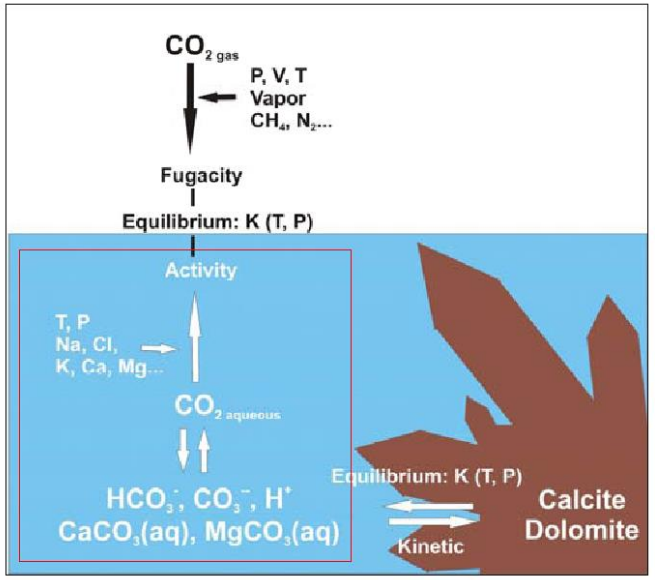
$\mathbf{F}^h = \sum_\beta h_\beta \mathbf{F}_\beta$ = advective mass flux over phases

Heat accumulation term in a multiphase system

$$M^h = (1-\phi)\rho_R C_R T + \phi \sum_\beta S_\beta \rho_\beta u_\beta$$

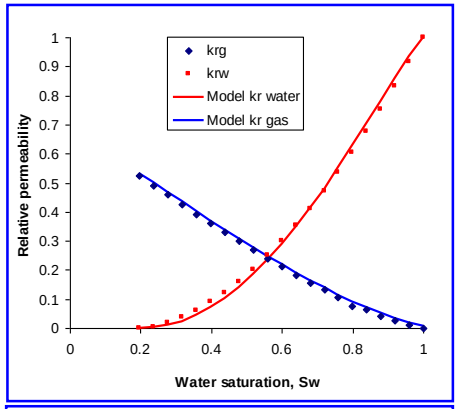
Modelling of chemical processes in the reservoir

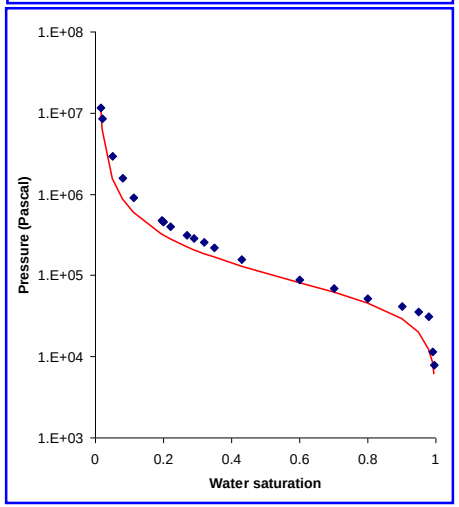
- Gas phase behavior (pressure/fugacity)
  - Gas mixing (Equation of state…)
  - …
- Liquid/gas Equilibrium
- Aqueous phase behavior
  - Chemical speciation in solution
  - Activity model (B-dot, Debye-Huckel, Pitzer…)
  - …
- Liquid/solid equilibrium
  - Dissolution/Precipitation Reactions
    - Equilibrium
    - Kinetic constraints
- Solid phase behavior
  - Variation of the reactive surface of minerals
  - Porosity/permeability variations
  - …

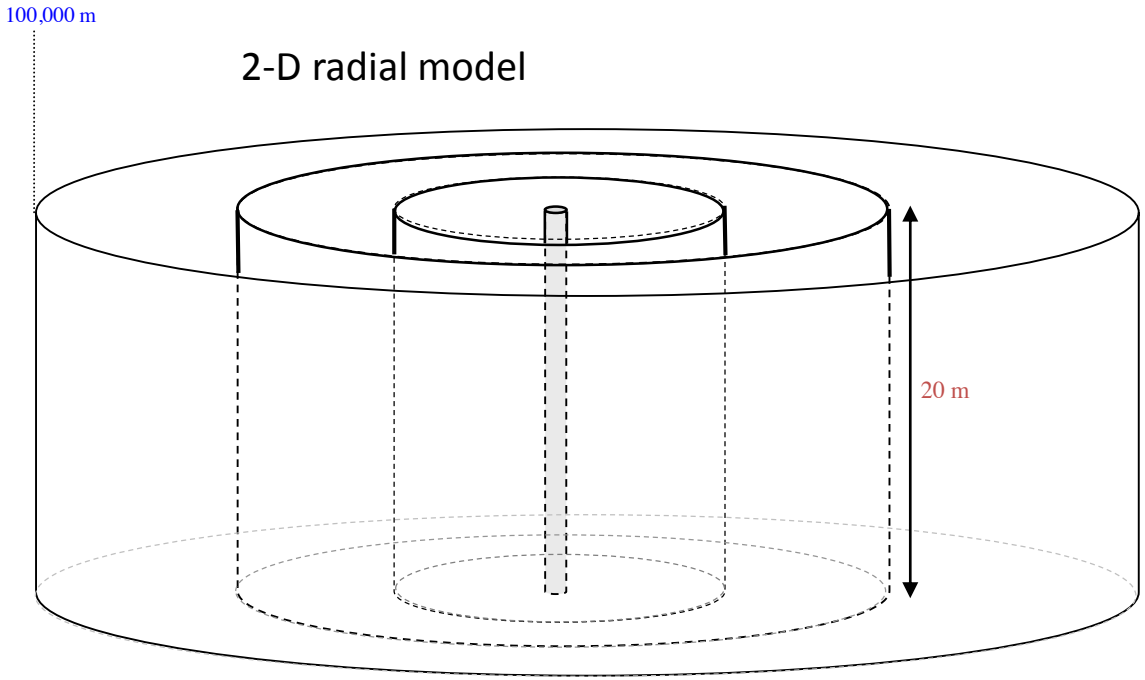


Miri et al., Int. J. Greenhouse Gas Control, 2016

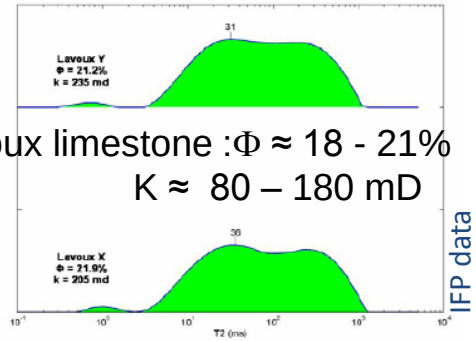
Simulation hypothesis: numerous parameters







Mineral composition (volumetric fraction)	
Calcite	0.70
Disordered dolomite	0.10
Siderite	0.05
Illite	0.05
Albite	0.05
K-feldspar	0.05



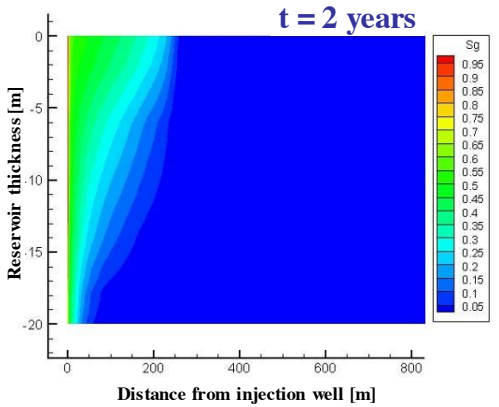
Lavoux limestone : $\Phi \approx 18 - 21\%$
$K \approx 80 – 180$ mD

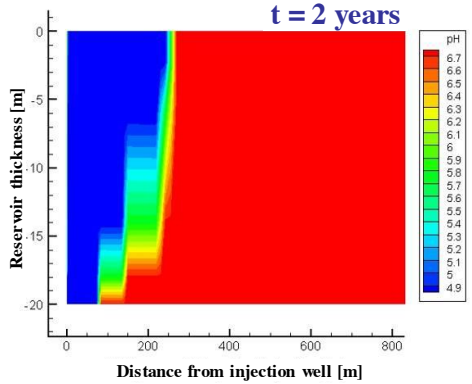
IFP data

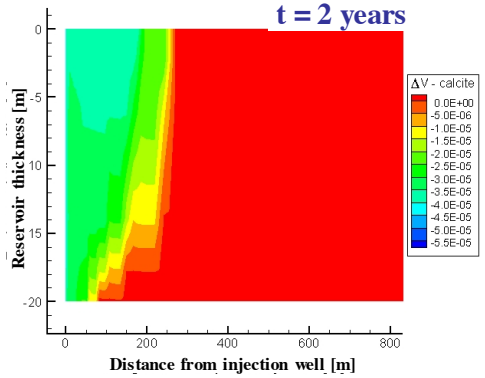
Initial temperature = 75°C
Initial pression = 180 bar

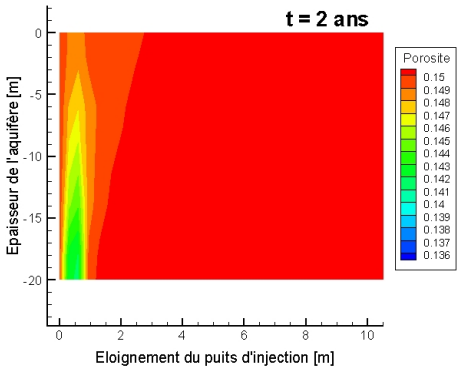
Température (°C)	74.2
TDS (g/kg H_2O)	5.6
pH	6.7
Alcalinité	427
Na	1794
K	35.2
Ca	148
Mg	55.9
Li	0.8
Al	0.002
Fe	1.0
Cl	2485
SO_4	633.6
SiO_2	41.4
HS	11.9

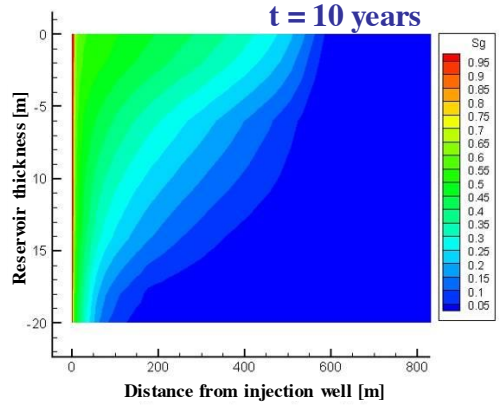
Simulations results (at reservoir scale) : gas saturation, pH, calcite content, porosity

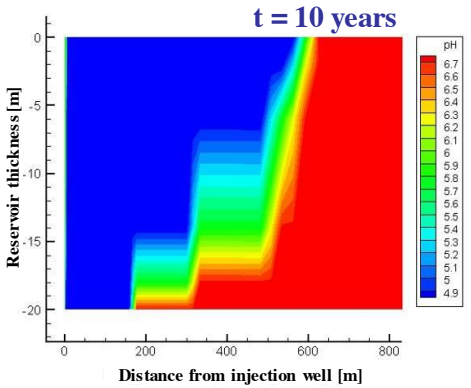


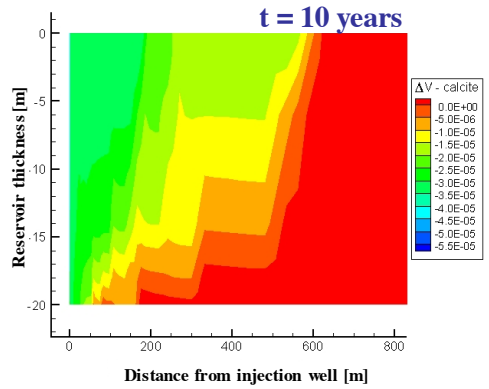


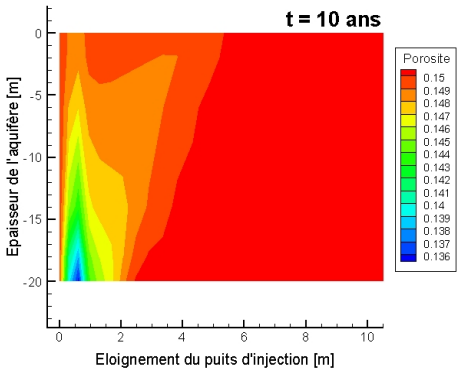












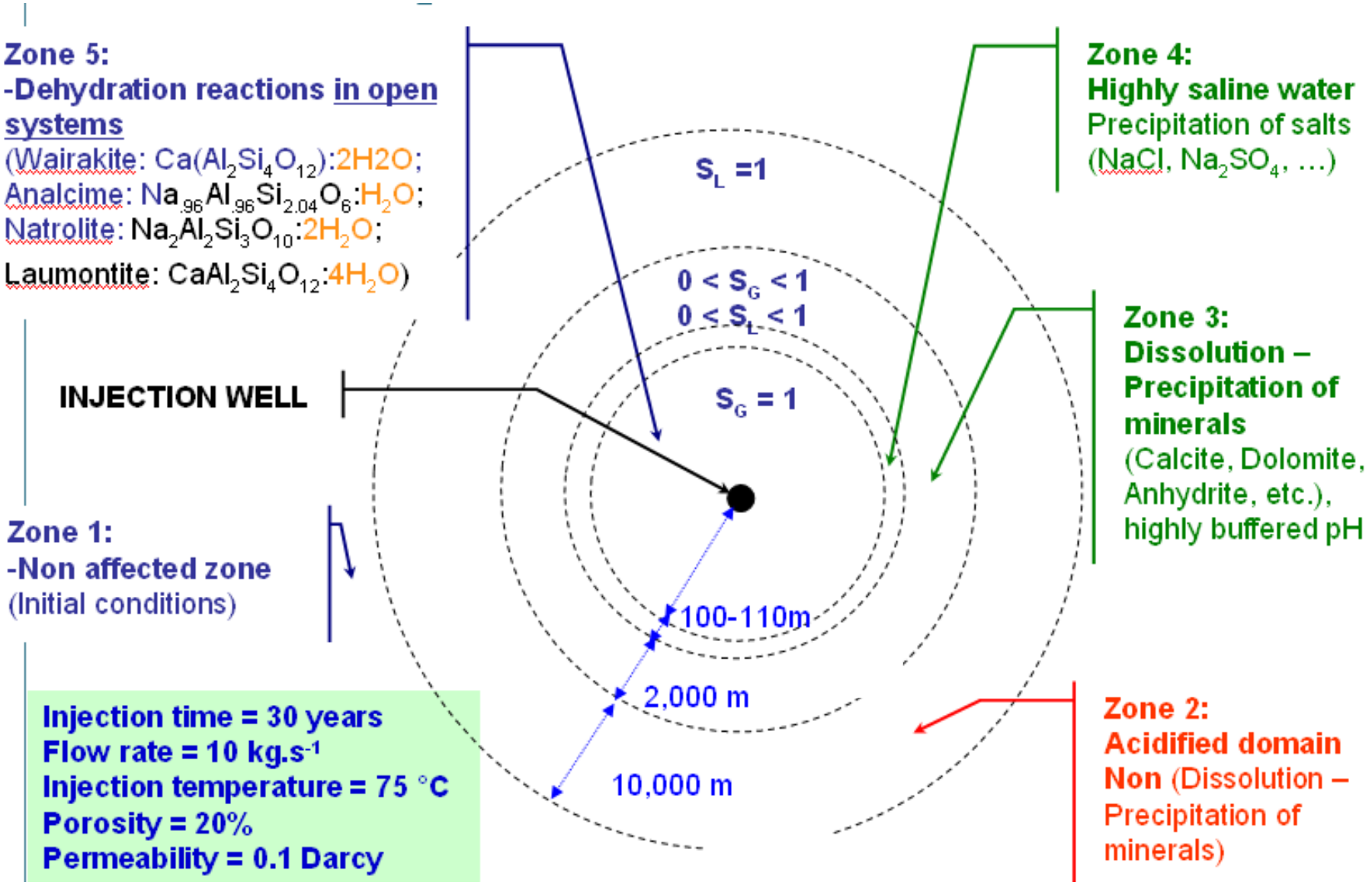
- Gas extension around the injection well
- Upward moving due to density effects

- pH decrease due to CO_2 dissolution
- pH controlled by calco-carbonique equilibrium

- Calcite dissolution due to water acidification

- Porosity variations because of mineral dissolution

Main physical and chemical processes impacting the near-well zone



Azaroual et al, 2007;
André et al, 2008

Modelling of Thermal Processes during CO_2 injection in deep carbonated aquifers

- Heat transfers between the reservoir and caprock (petrophysic property)
- Heat of CO_2 dissolution (thermodynamic property) :
  - $h_{CO2,aq} = h_{CO2} + h_{dis}$ is the specific enthalpy of aqueous (dissolved) CO_2, which includes heat of dissolution effects that are a function of temperature and water salinity
- Heat energy of water vaporisation (thermodynamic property)
- Joule-Thomson Effect (thermodynamic property) : isenthalpic expansion of real gases

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial P}\right)_H \approx \frac{\Delta T}{\Delta P},$$

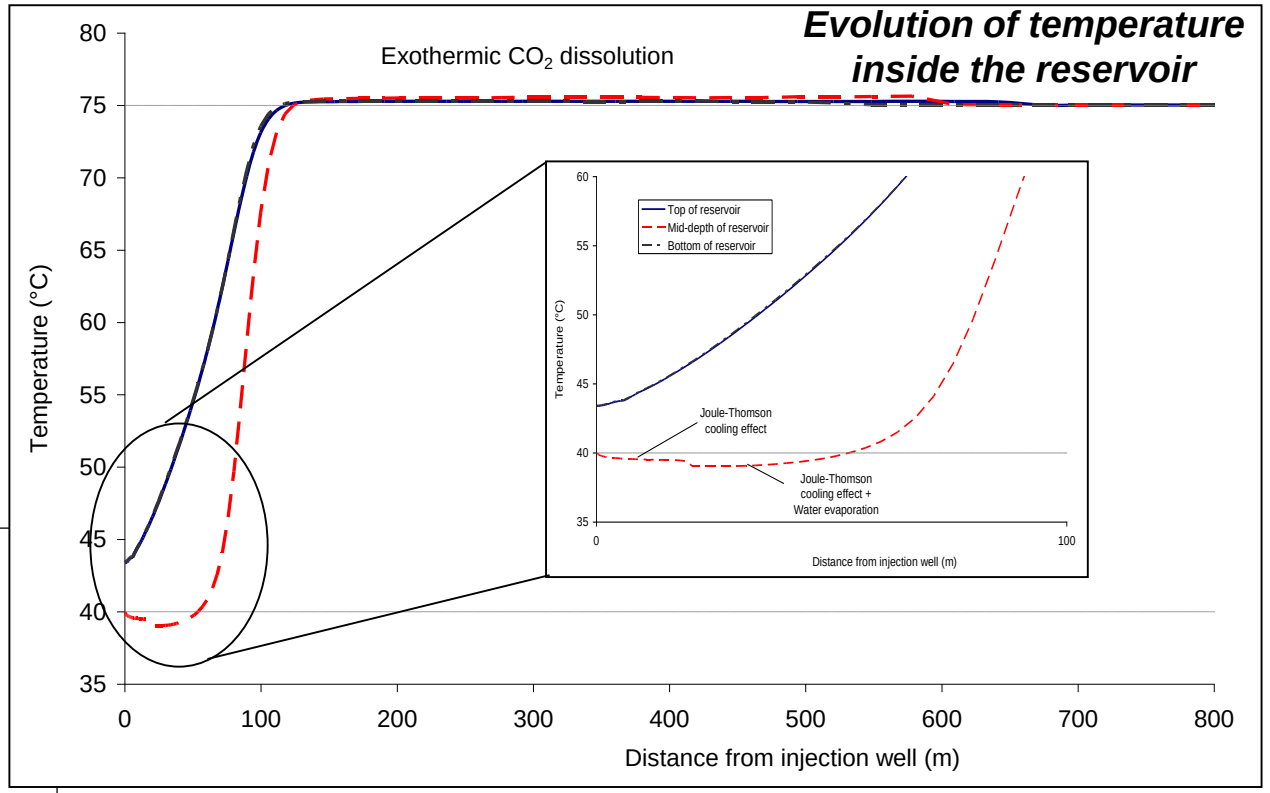
- Injection temperature (anthropic)

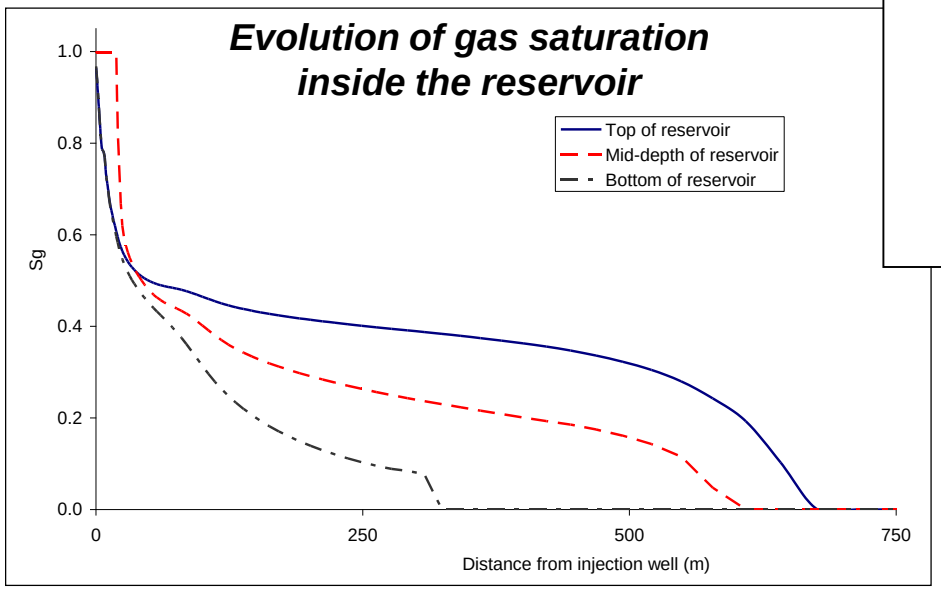
Well injectivity during CO_2 injection in deep carbonated aquifers : Thermal impacts

Initial T = 75°C
Injection T = 40°C
Injection period : 300 days

Reservoir thickness = 20 m

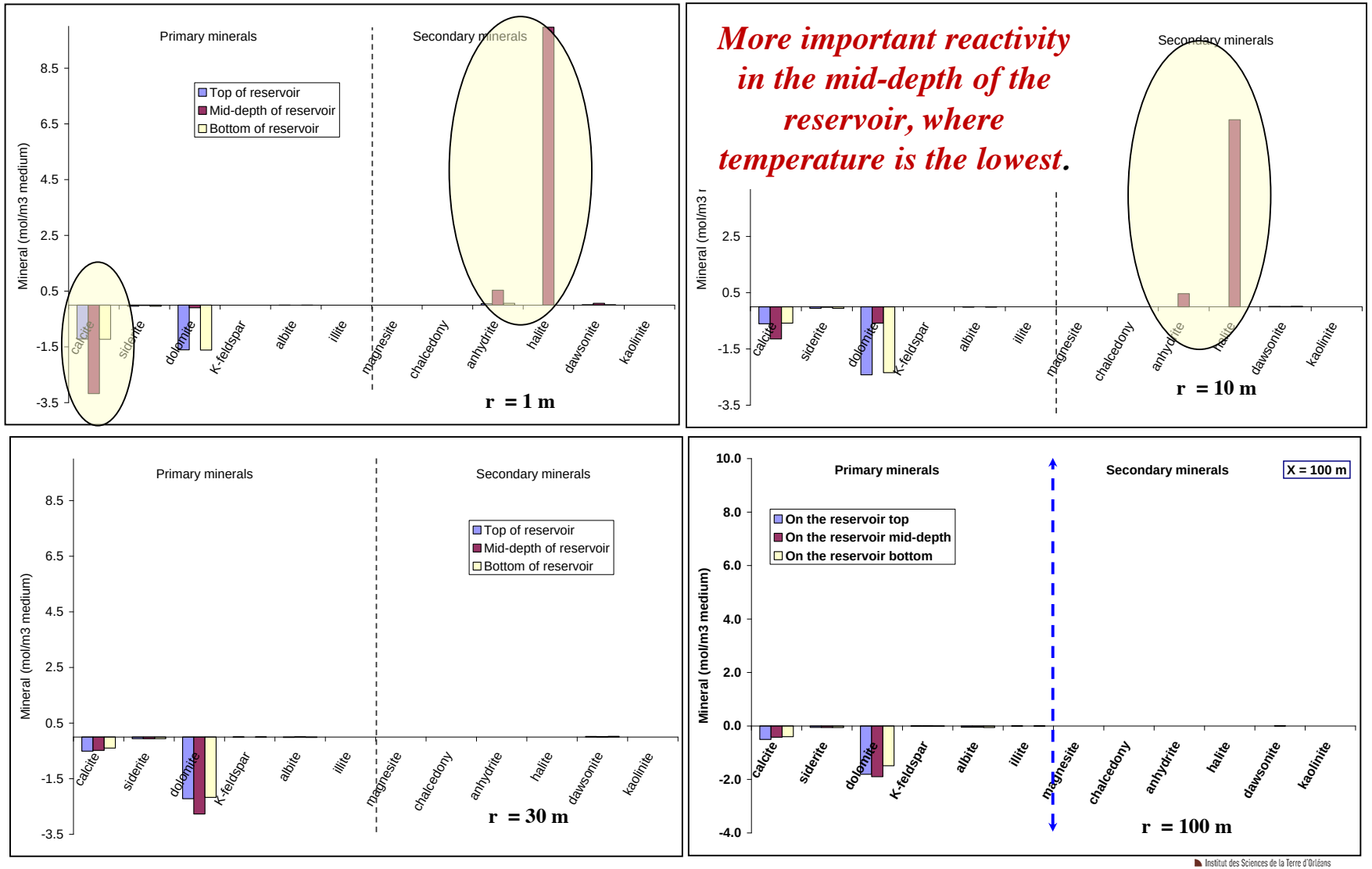
Injection rate = 20 kg s^{-1}





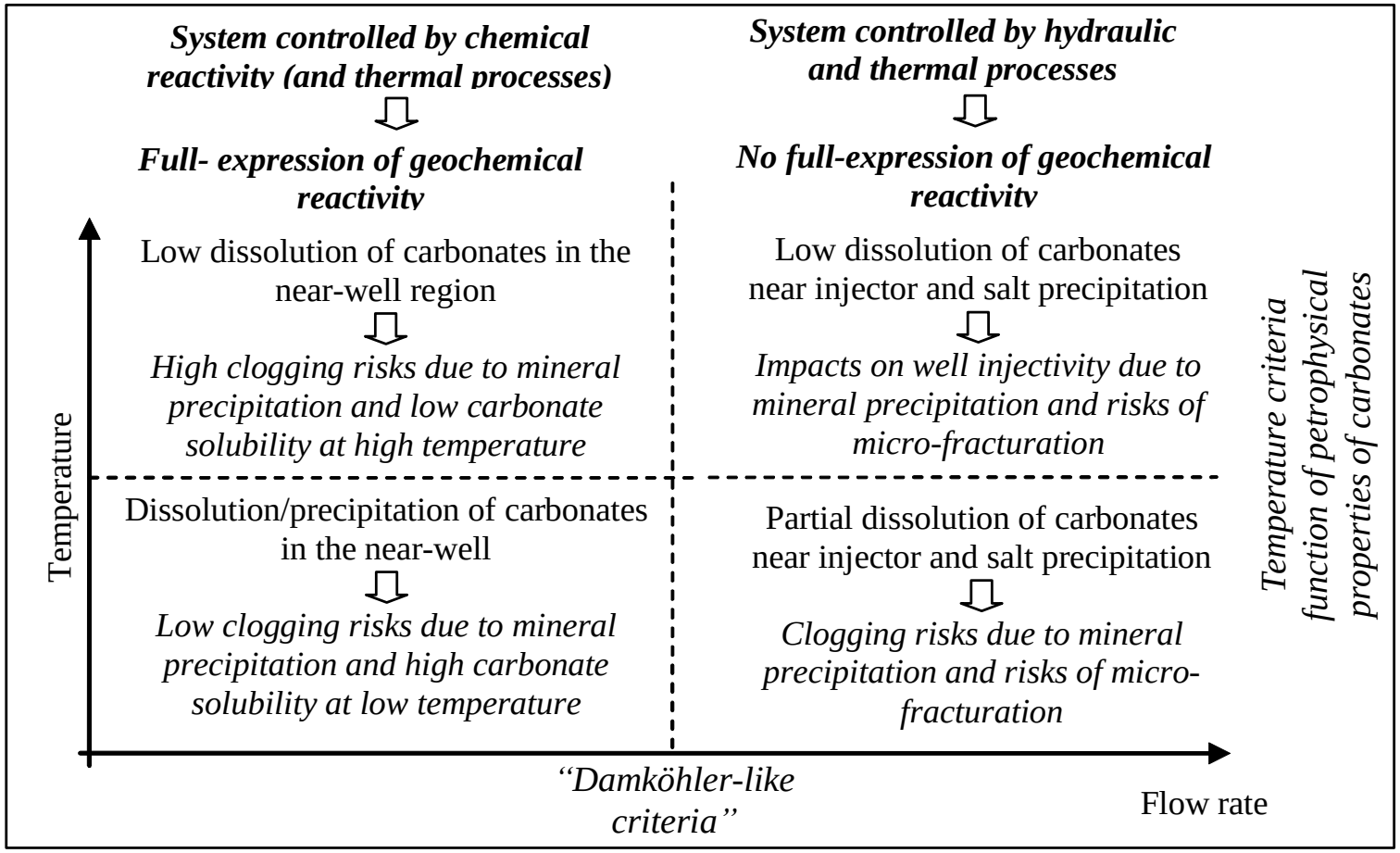
(André et al., TIPM, 2010)

Well injectivity during CO_2 injection in deep carbonated saline aquifers: Thermal effects (Impact on geochemistry)



(André et al., TIPM, 2010)

Well injectivity during CO_2 injection in deep carbonated saline aquifers



=> Injection scenarios versus injection temperature and supercritical CO_2 flow rate in carbonate reservoirs.

(André et al., TIPM, 2010)

Overview of the presentation

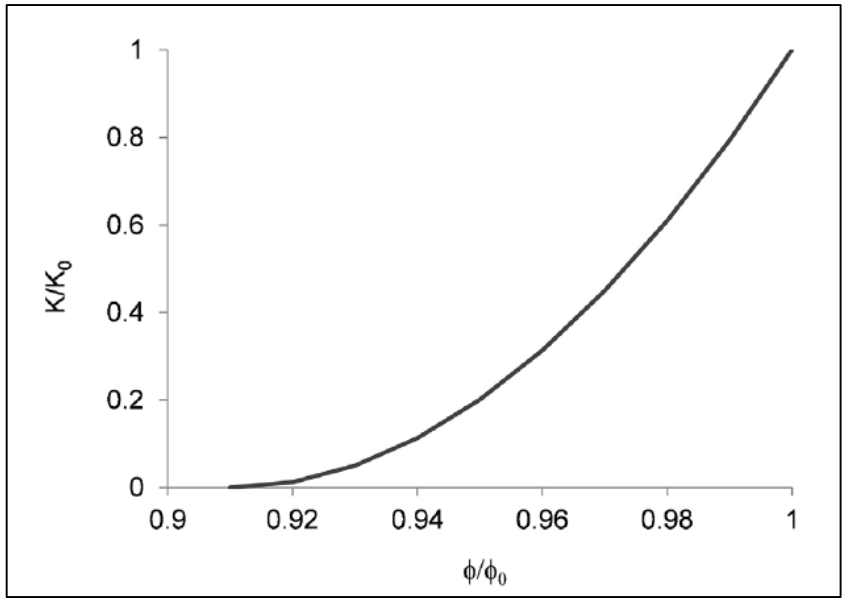
- **Biochemical reactions**
  - An experimental and modelling coupled approach – Application to denitrification
- **Multiphasic systems**
  - The necessity to use coupled approaches – Application to CO_2 storage in deep geological reservoirs
- **Conclusions and Perspectives**

CONCLUSIONS AND PERSPECTIVES

Coupled chemical-transport codes are useful tools to simulate the main processes affecting fluids, solid and gases in subsurface environments.

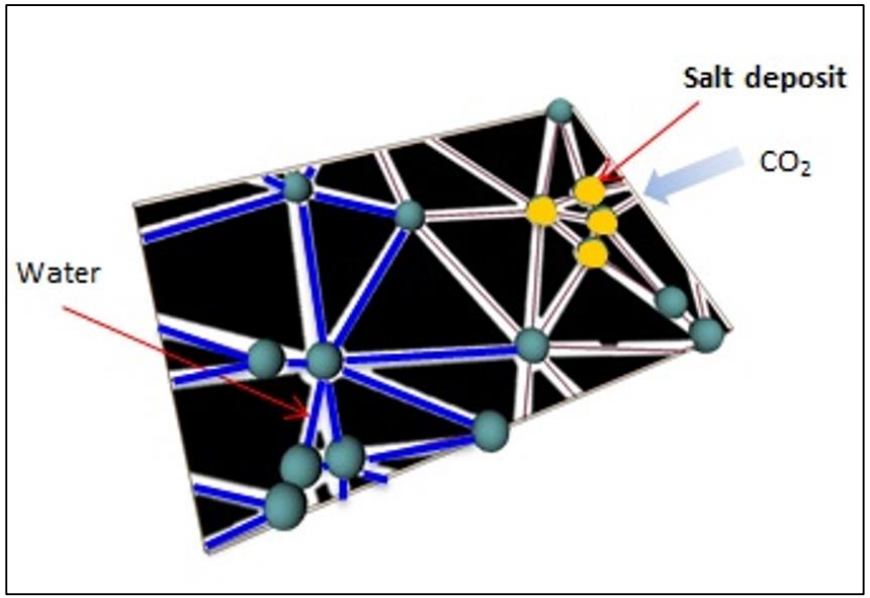
However, we could go further if some locks were studied as:

- ***The modelling of porosity variations***, related to chemical reactivity, and the porosity/permeability relationship must be improved (k-Φ relationship)



Relationship between porosity and permeability reduction for Vosges sandstone

(André et al., Int. J. Greehouse Gas Control, 2014)



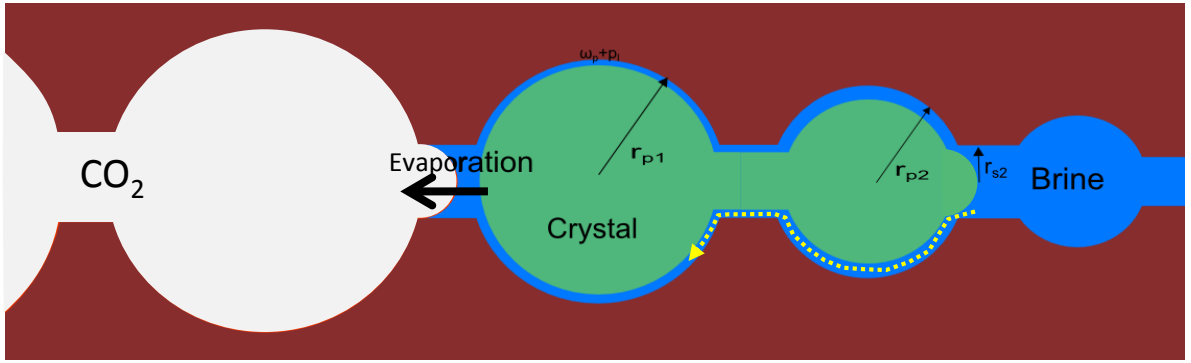
The *Geological Labs on a Chip* (GLoC) concept for studying key processes of multiphase reactive transport

CONCLUSIONS AND PERSPECTIVES

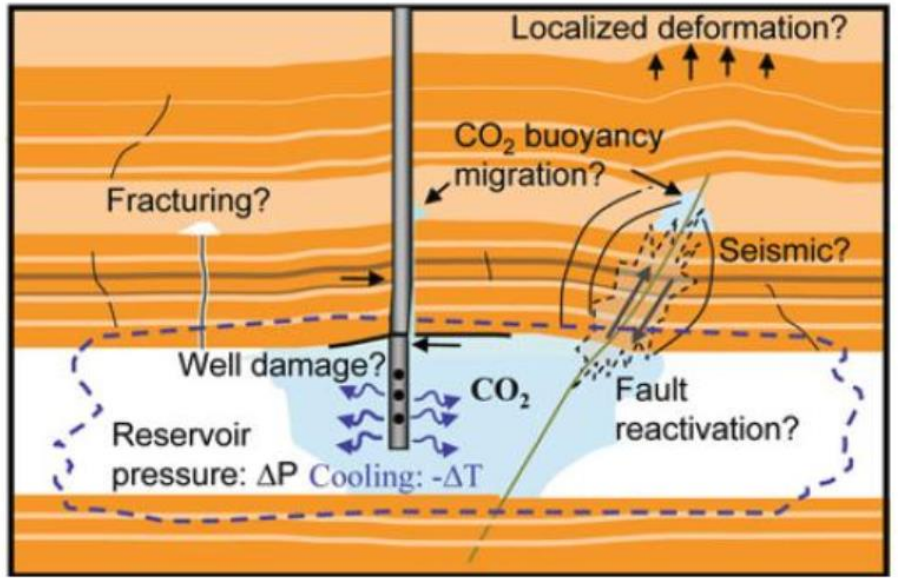
Coupled chemical-transport codes are useful tools to simulate the main processes affecting fluids, solid and gases in subsurface environments.

However, we could go further if some locks were studied as:

- ***The coupling of chemical reactions with mechanical properties.*** *Or how the mineral dissolution or precipitation can modify the mechanical properties of rocks ?*



(Osselin et al, Europ. Phys. J. Appl. Physics, 2013)



(Rutqvist, 2012)

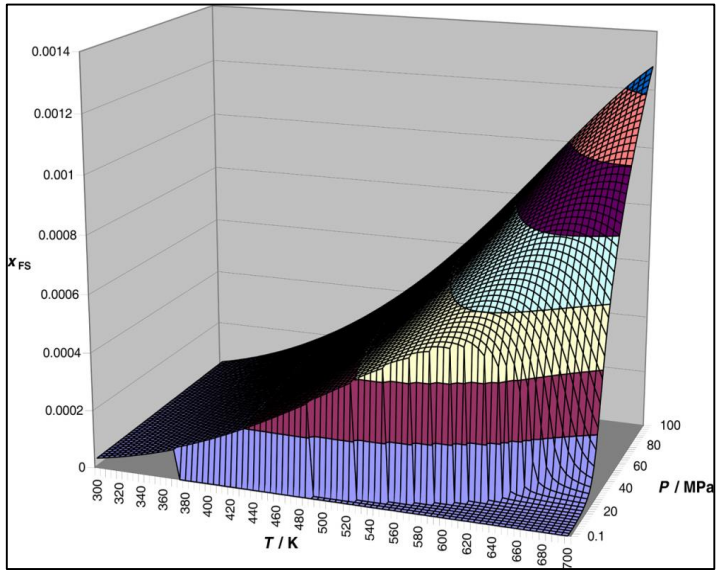
⇨ Brine concentration at equilibrium with slit 2 > brine concentration in pore *i*
⇨ Ionic diffusion through films
⇨ Growth of salt crystals in pores
⇨ Generation of overpressure

CONCLUSIONS AND PERSPECTIVES

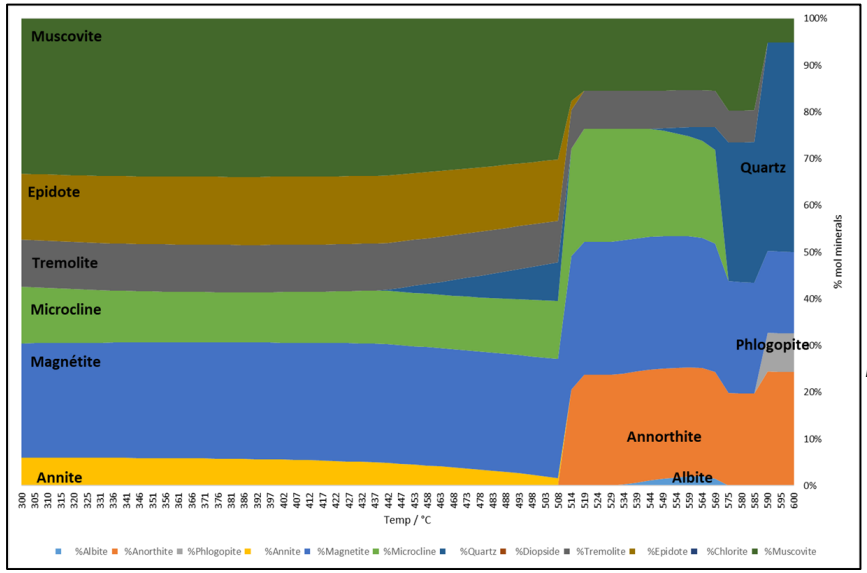
Chemical-transport coupled-codes are useful tools to simulate the main processes affecting fluids, solid and gases in subsurface environments.

However, new numerical developments are needed to go further :

- ***The extension of thermodynamic databases to high temperatures.*** Resources exploitation need to go deeper and deeper : geothermal energy, energy storage…



Silica solubility up to 700°C and 100 bars



Mineral changes of a rock in contact with 1 molal NaCl solution during the cooling from 600 °C to 300°C

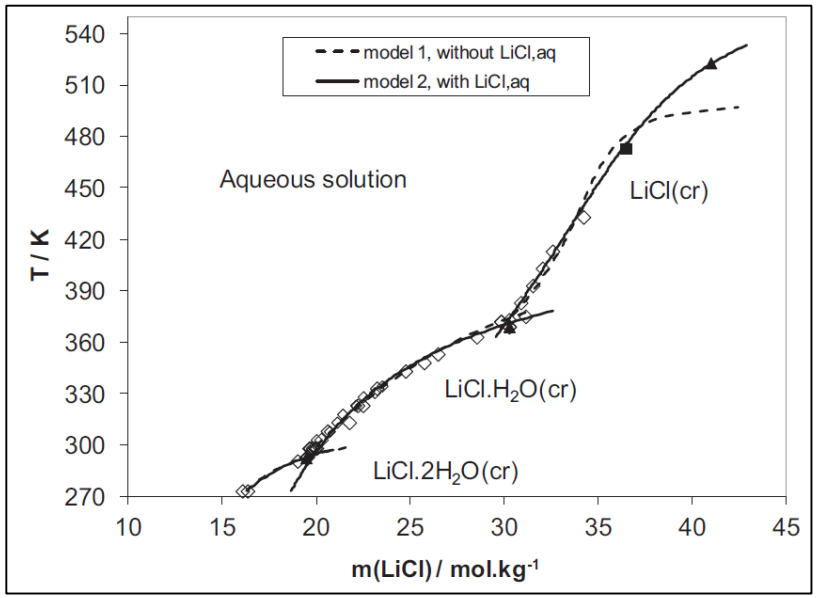
CONCLUSIONS AND PERSPECTIVES

Chemical-transport coupled-codes are useful tools to simulate the main processes affecting fluids, solid and gases in subsurface environments.

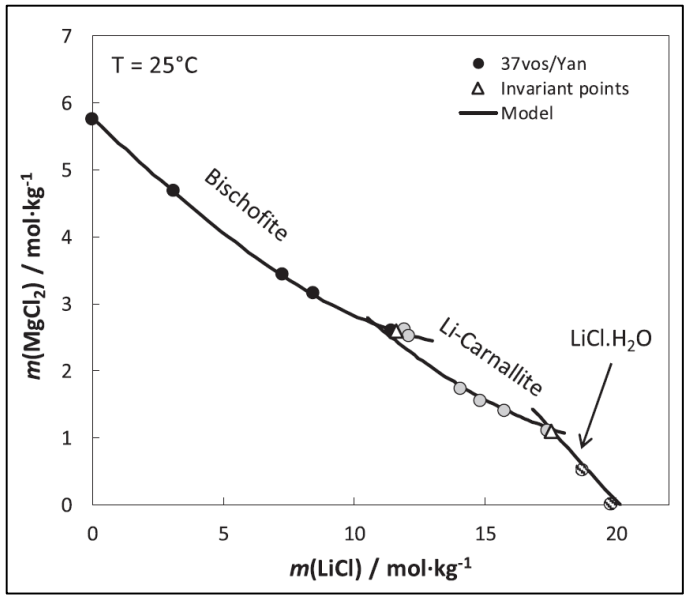
However, new numerical developments are needed to go further :

- ***The chemical modelling of salted systems***. Specific thermodynamic models are developed for brines but improvements are needed, especially in aluminum, iron and silica-bearing systems.

Development of specific thermodynamic databases for the exploitation of lithium in brines



(Lassin et al., Am. J. Sci., 2015)



(Lassin et al., CALPHAD, 2018)

THANK YOU FOR YOUR ATTENTION

QUESTIONS ?

INSTITUT CARNOT brgm

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