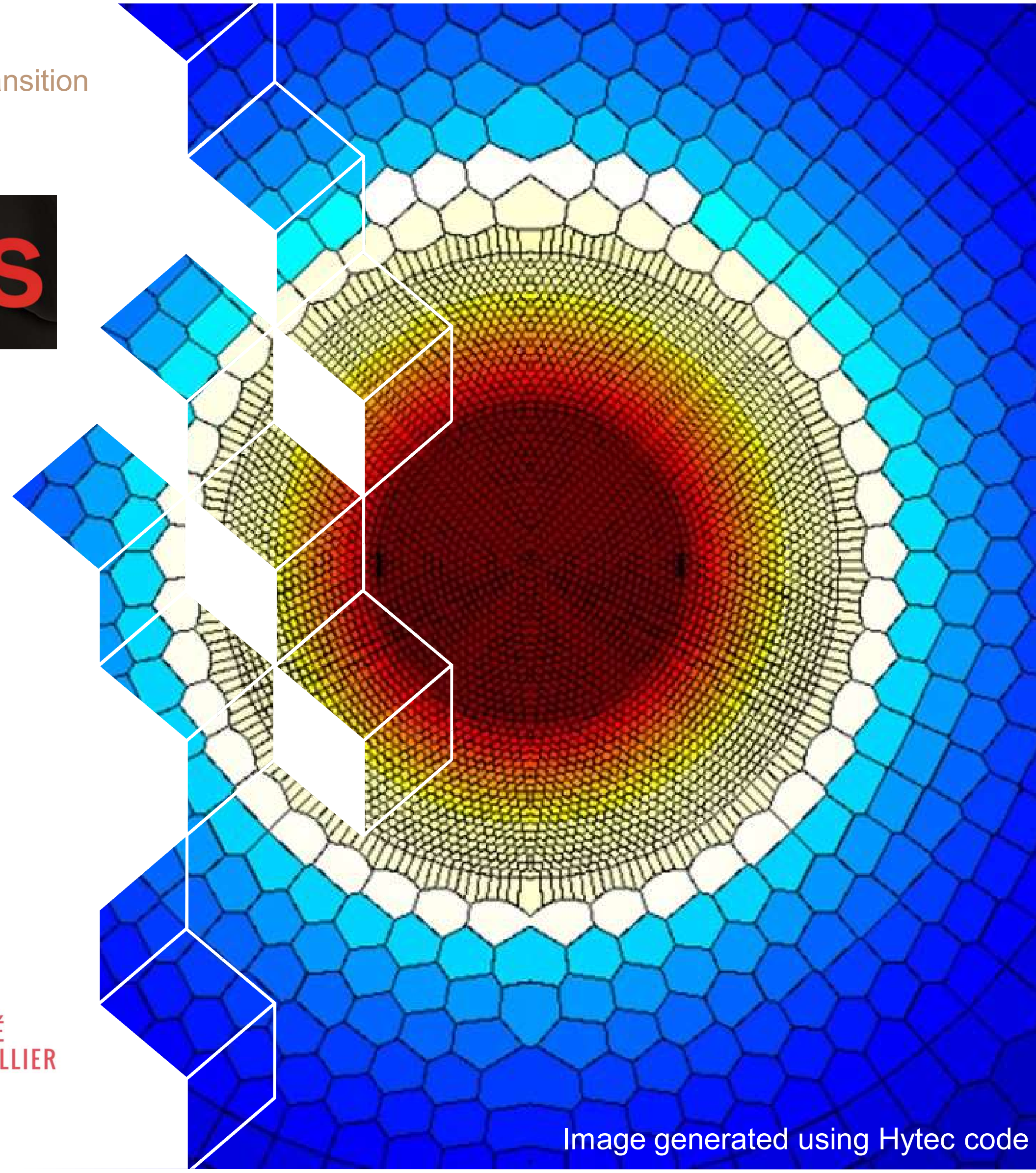
3rd Summer School on nuclear and industrial glasses for energy transition

sumglass

September 25-29th 2023

Geochemical Modeling of Glass Alteration

Pierre Frugier (CEA ISEC, France)



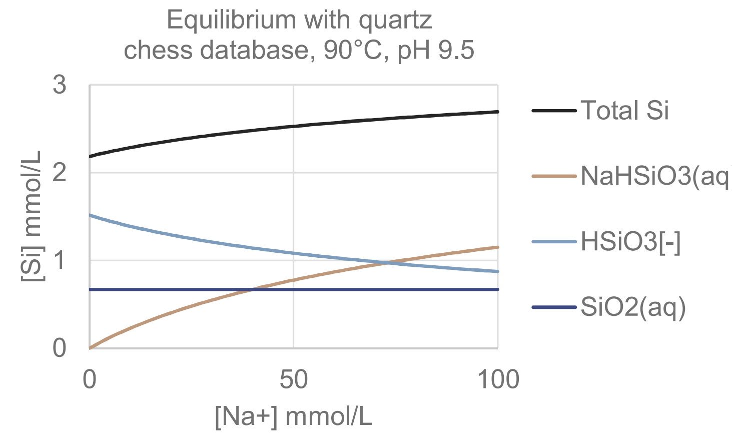
Geochemical Modeling of Glass Alteration

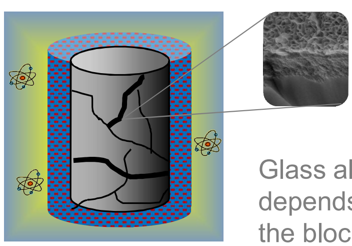
- **Why ?**

  - Precipitation of secondary minerals: a key process
    Fe silicates, Mg silicates, Ca carbonates…

  - Fluid speciation is required to predict concentrations

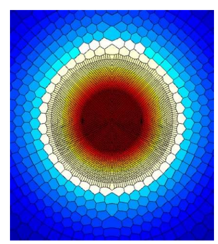
  - Transport in the fluid by diffusion/convection controls the degree of interaction between the glass and its environment.

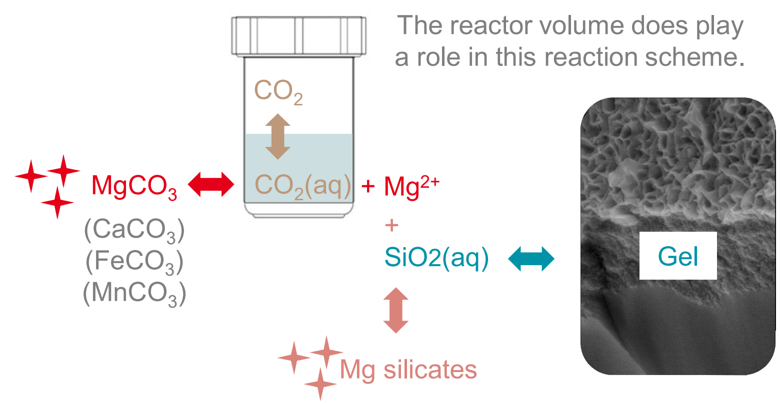




Glass alteration strongly depends on its position in the bloc / pile of grains

Geological disposal is an open system

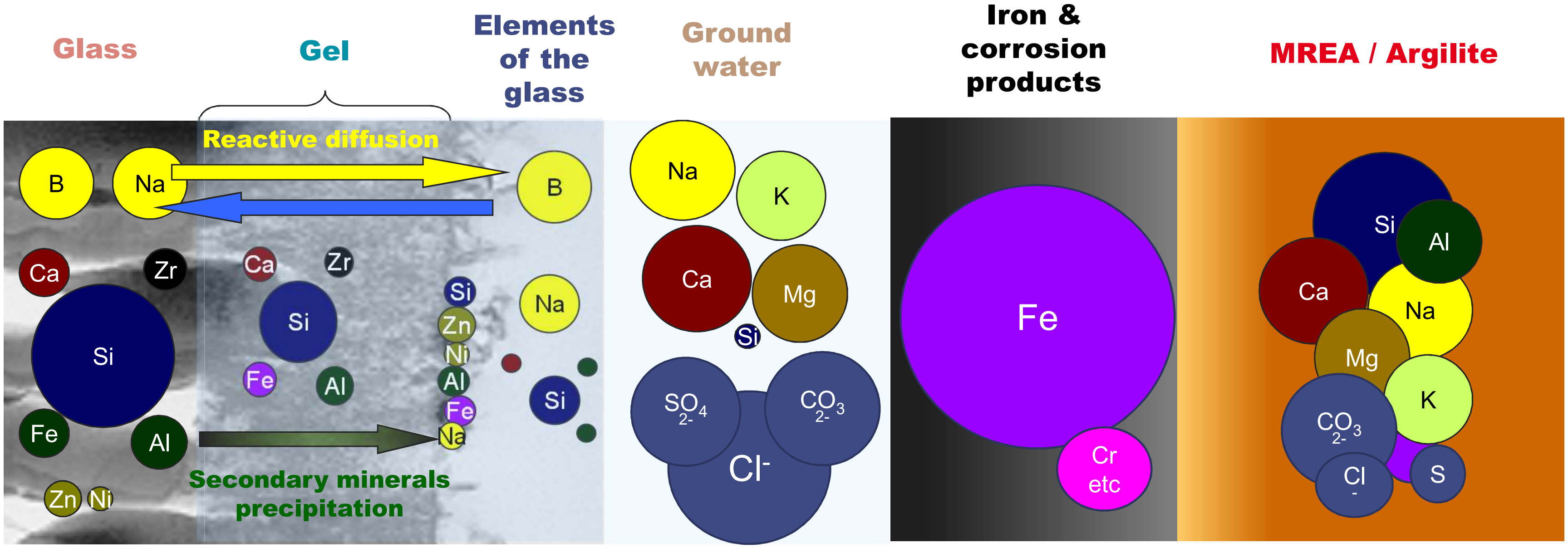




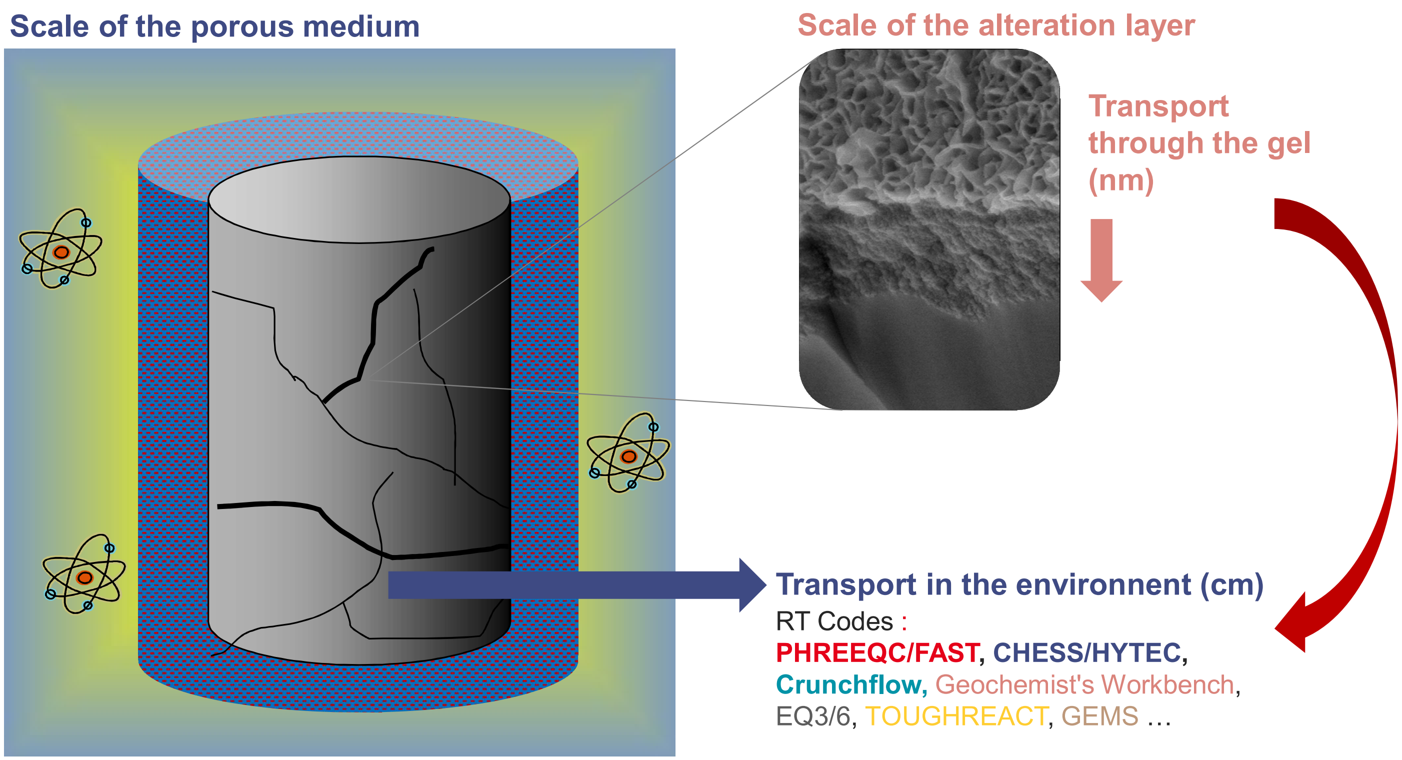
  - Prediction of gases (CO_2, H_2) is required

Geochemical Modeling of Glass Alteration

- **Why ?**
  - Reactive Transport Codes handle complex chemical systems



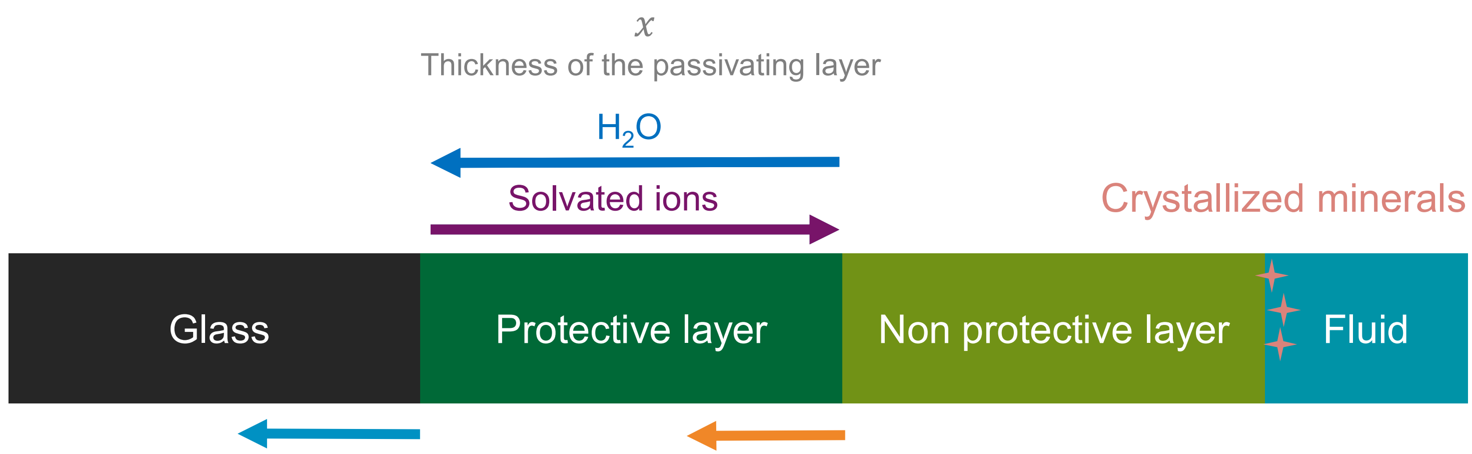
How taking into account the transport through the gel in a RT Code ?



GRAAL enables a **change in scale** thanks to an **implicit modeling** of diffusion through the gel.

GRAAL enables the **implementation of the flux of elements** diffusing through the gel in the RT code.

GRAAL Equations



Glass alteration kinetics decreases with the increase in the thickness of the protective layer (x)

$$r_1 = \frac{A}{x}$$

Cf. Fick's law $J = -D\frac{\Delta C}{x}$

Dissolution kinetic of the protective layer

$$r_2 = k\left(1 - \frac{Q}{K}\right)$$

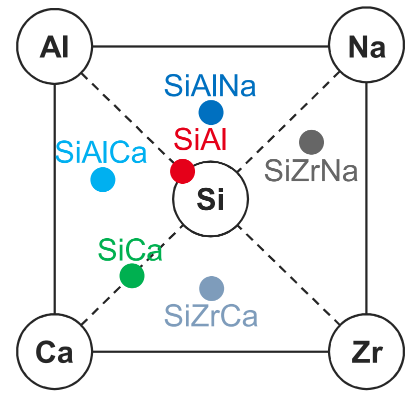
Cf. Aagaard & Helgeson

* Frugier et al. JNM 2008, 2009
Frugier et al. NPJ 2018

Kinetic parameters D (A) and k are functions of pH and T, K is a function of T

GRAAL : gel composition and solubility

- **Gel is described with end-members**
  - Each end-member has a composition
  - Each end-member has a logK(T) value
  - The global gel composition is obtained by summing each end-member



- **End-members quantities are used to calculate the thickness (x) of the gel, which is then used to calculate (r_1)**

[end-member] concentration divided by Surface → thickness of the gel x → r_1

A little bit of history

Concept & Equations

Implementation
CHESS/HYTEC

Basis
JNM 2008

Fluid Volume
JNM 2009

Glass Composition
Chem. Geol. 2010

Analytic Equations
JNM 2010

Hydromagnesite
JNM 2012

Ground water
JNM 2012

Magnetite
JNM 2013

Diffusion Cell experiments
JNM 2013

Dolomite
Appl. Geochem. 2013

Zeolite
JNM 2017

Clayed fraction
Appl. Geochem. 2018

Implementation in other RT codes
Crunchflow & PHREEQC

Glass Composition
NPJ 2018

Radioactivity
Internal doc.

2006 GRAAL 2023

2019 GRAAL 2 …

Concept & Equations
Internal doc.

Implementation
CHESS/HYTEC

AVM Glass
Internal doc.

AVM Glass + Mg
Internal doc.

SiBNaAl glass
Internal doc.

Siderite
Internal doc.

Python & JupyterLab

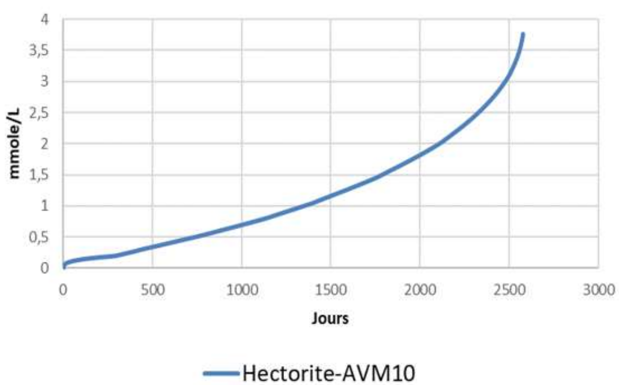
Many people deserve to be warmly thanked for their contributions and support around GRAAL, and we should also include all our partners from ORANO, EDF and ANDRA. Among them, is …Arena, Ayral, Bildstein, Bonin, Chave, Corvisier, Coste, Debure, Delcroix, De Windt, Ducasse, Fleury, Fournier, Frugier, Geiger, Gin, Godon, Jollivet, Lartigue, Minet, Noiriel, Martin, Rajmohan, Sessegolo, Thien, Verney-Carron…

What is new with GRAAL2 ?

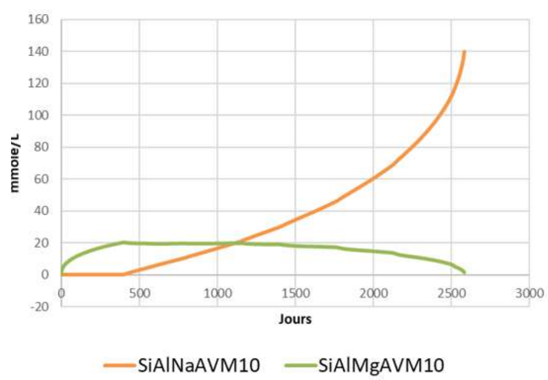
- **Generalized passivation equation**
  - A diffusion coefficient is affected to each end-member
  - Thus, there is feedback from the gel composition on the transport properties of the gel.
  - Implemented in CHESS/HYTEC
  - e.g. AVM10 glass

$$r_1 = \frac{r_h}{1+\left(\sum_1^n \frac{x_i}{D_i}\right)\frac{r_h}{\frac{\pi}{2}}} \sim \frac{1}{\left(\sum_1^n \frac{x_i}{D_i}\right)\frac{2}{\pi}}$$

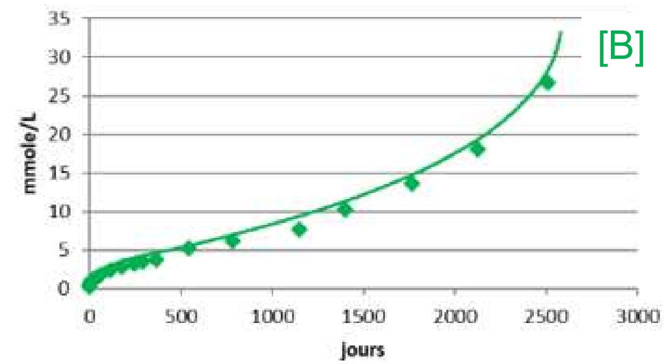
Mg precipitates as hectorite



Mg is replaced by Na in the gel



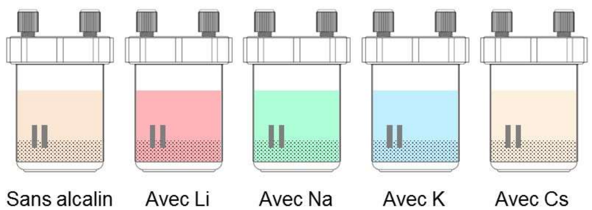
Alteration increases because Na-rich gel is less passivating than Mg-rich gel

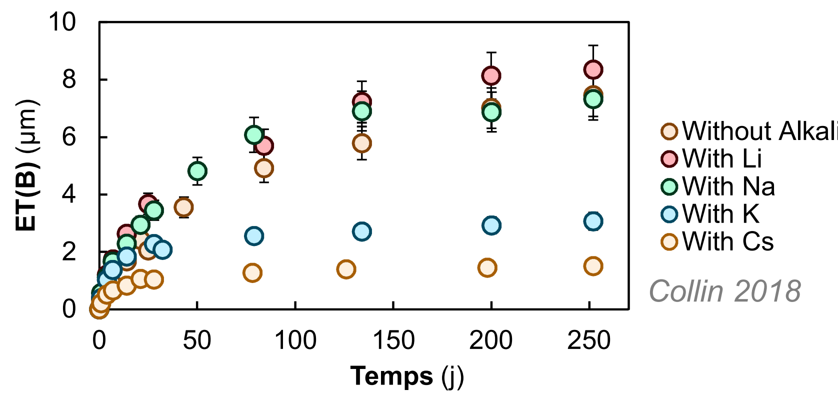


What is new with GRAAL2 ?

- **Generalized passivation equation**
  - Other evidence that the apparent diffusion coefficient is influenced by the gel composition?
    - Chave 2010 for Calcium
    - Thien 2012 and Frugier & Godon 2018 for Magnesium
    - Collin 2018 for Alkalis.

pH 7, 90 °C, saturated with respect to SiO_2
No alkali added or ~20 mmol·L^{-1} of XCl
(X = Li, Na, K ou Cs)



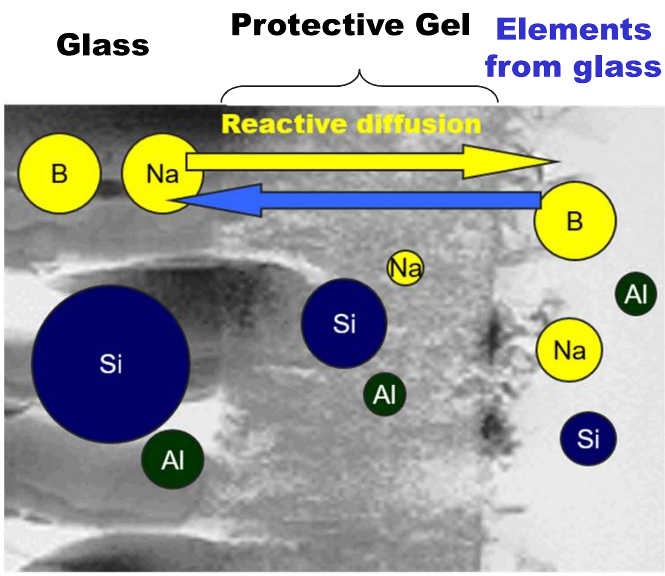


Collin 2018

An exogenous ion can become part of the gel composition and significantly alter its apparent passivation coefficient by several orders of magnitude

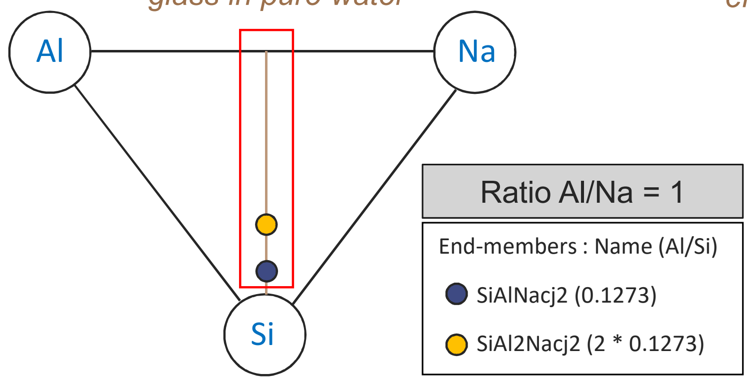
What is new with GRAAL2 ?

- **End-members number is free**
  - It is possible to capture the entire chemical complexity of the gel, subject to having sufficiently precise and abundant data.
  - Bounding the gel composition is required but a limited number of end-member is already efficient.
  - Gel must be able to evolve accounting elements provided by the environment.

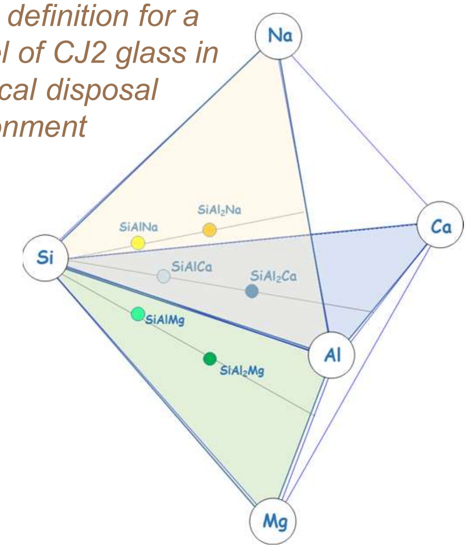


Case of cj2 (4-oxide glass)

End-members definition for CJ2 glass in pure water



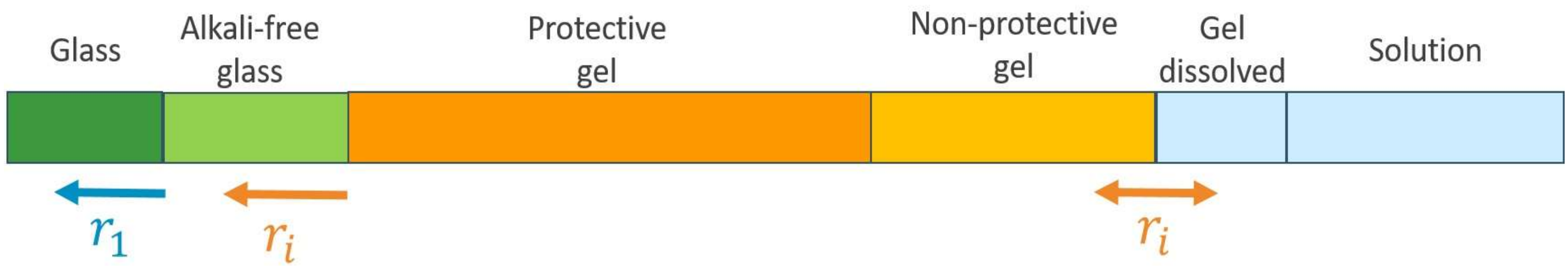
End-members definition for a predictive model of CJ2 glass in the geological disposal environment



What is new with GRAAL2 ?

- **Alkali-free glass zone can be taken into account (GRAAL 2.2)**
  - By hypothesis it occupies the volume of the altered glass.
  - It is meant to reorganize into a gel.
  - It contributes to passivation like any other gel end member thanks to the generalized passivation equation.

$$r_1 = \frac{r_h}{1+\left(\sum_1^n \frac{x_i}{D_i}\right)\frac{r_h}{\frac{\pi}{2}}} \sim \frac{1}{\left(\sum_1^n \frac{x_i}{D_i}\right)\frac{2}{\pi}}$$



What is new with GRAAL2 ?

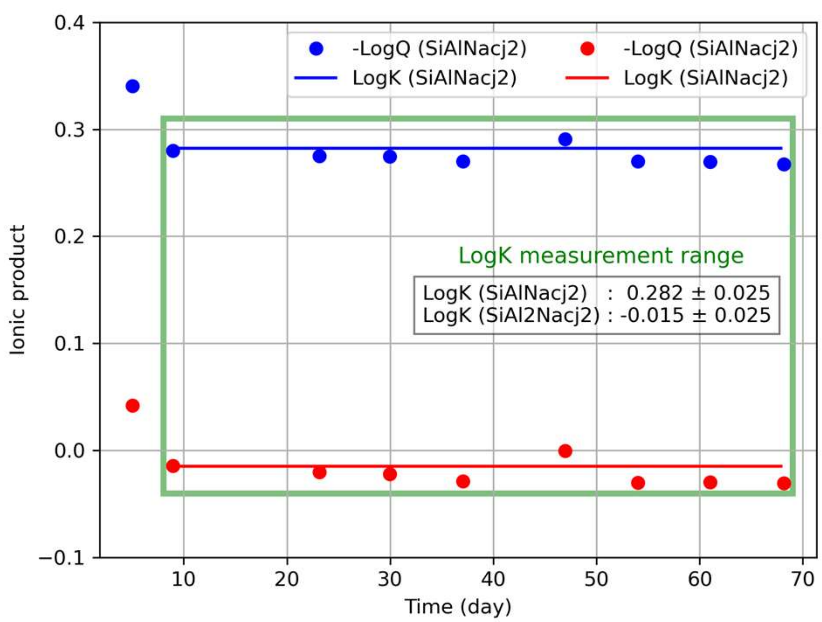
- **GRAAL2 allows for a volume assessment, not just a quantification of matter**
  - Subject to certain parameters of the meso and micro scale being known
    - Molar volume of the gel
    - Volume occupied by bound water
    - Volume occupied by water in closed porosity
    - Maturation of the gel (e.g. effect of network strengtheners)
  - A density threshold at which the gel becomes protective can be set
  - Those GRAAL2 imput parameters can be output parameters from atomistic models
  - Volume assessment allows for the reconstruction of the actual thickness of the gel and, consequently, a better estimation of the apparent diffusion coefficients.

$$r_1 = \frac{1}{\left(\sum_1^n \frac{x_i}{D_i}\right)\frac{2}{\pi}}$$

What is new with GRAAL2 ?

- **GRAAL2 comes with Python & Jupyterlab** → Methodology improvement
  - Parameter quantification can be automated for greater objectivity

logK



➢ Geochemical calculations showing the evolution of ionic products associated with the end member equations

SiAlNacj2 = 0.2231 H4(SiO4), 0.0284 Al[3+], 0.0284 Na[+], -0.1136 H[+], -0.3894 H_2O

logQ = $H4(SiO4)^{0.2231}$ * $Al[3+]^{0.0284}$ * $Na[+]^{0.0284}$ * $H[+]^{-0.1136}$ * $H_2O^{-0.3894}$

➢ Analysis of temporal trends in ionic products

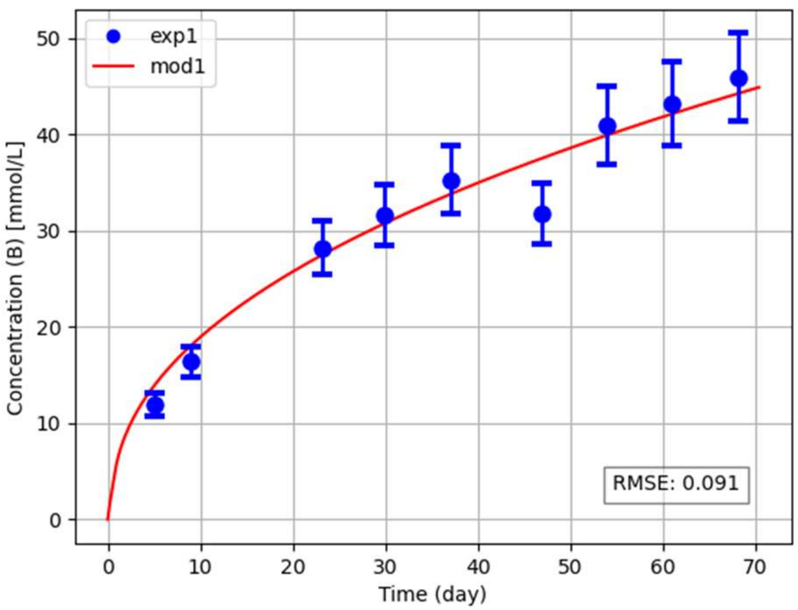
➢ LogK are chosen to ensure equilibrium with the solutions in which the end-members are meant to be present

Ph.D. Maxime Delcroix

What is new with GRAAL2 ?

- **GRAAL2 comes with Python & Jupyterlab** → Methodology improvement
  - Parameter qualification can be automated for greater objectivity

Diffusion coefficients



- Boron not consumed in gel formation, constantly increasing at a rate depending on the diffusion coefficient through the gel.

- The experimental boron concentration is used to determine the diffusion coefficient

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What is new with GRAAL2 ?

- **GRAAL2 comes with Python & Jupyterlab** → Methodology improvement
  - Uncertainties propagation

Δ Experimental data

based on 3σ

[3] ↓

Δ Modelling parameters

based on 3σ

[3] ↓

Δ Predictions

based on 3σ

Δ Si, Δ Na, Δ B: **Δ = 10%**

Δ Al: **Δ = 20%**

End-members solubility: **Δ = 0.025** (**ΔLogK**)

Diffusion through the gel: **Δ = 15-20 %** (**ΔDi**)

Δ Si: **Δ = ~20%**

Δ Na, Δ B: **Δ = ~10%**

Δ Al: **Δ = ~40%**

Δ Al/Si gel: **Δ < 10%**

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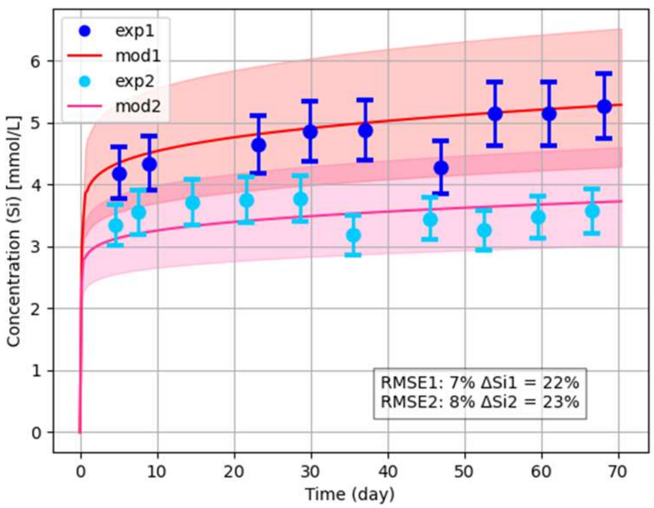
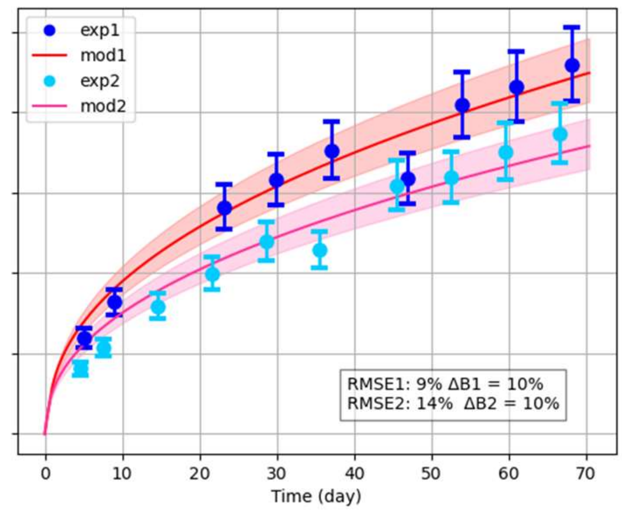
What is new with GRAAL2 ?

- **GRAAL2 comes with Python & Jupyterlab** → Methodology improvement
  - Comparison with **standard deviation** between the experimental data and the model **bundle of curves** → Qualification of the model.

Si



B



The **root mean square error (RMSE)** is used here to estimate how close the modelling results are from the experimental results.

$$RMSE = \sqrt{\frac{1}{N}\sum\left(\frac{V_{sim} - V_{exp}}{V_{exp}}\right)^2}$$

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What is next with GRAAL2 ?

FP3

- **GRAAL2 comes with Python & Jupyterlab**
  - Python environment makes it easier for any further improvement of the model.
  - The JupyterLab interface significantly speeds up the global modeling process.
  - It enables the application to a growing amount of experimental data.

It allows for parameterizing the entire domain of interest.

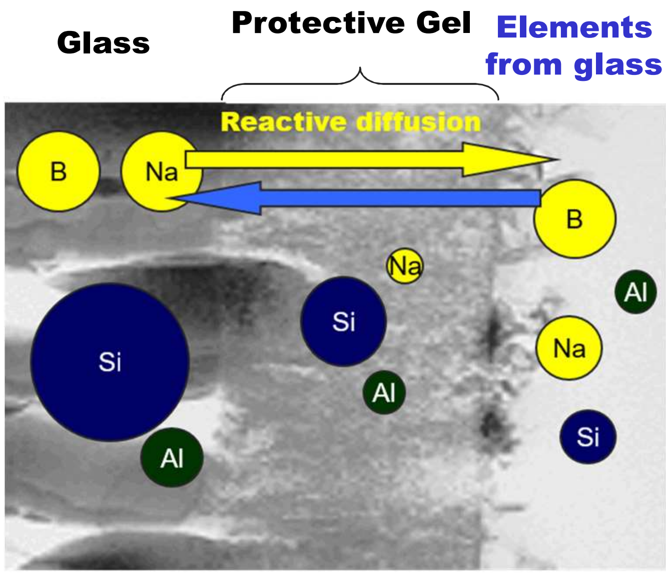
  - It helps limit human errors, leverage knowledge, and facilitates teaching.

Diapositive 17

FP3 FRUGIER Pierre; 19/09/2023

Some recent applications ?

- Ph.D. **Maxime Delcroix**



Working environment : cj2 (4-oxide glass)

CJ2	molar % of oxides
SiO2	65
Na2O	14
B2O3	17
Al2O3	4

cj2 glass composition

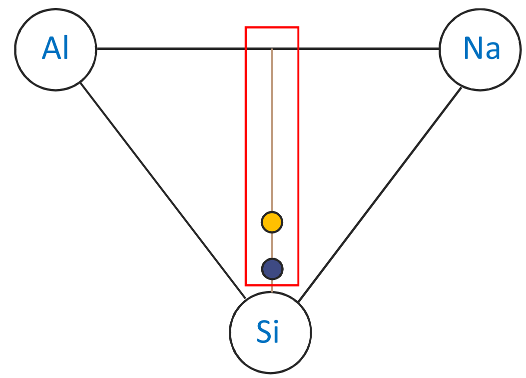
Gel = main element to be modelled

Revisiting the model's fundamental assumptions

- **Number of end-members:**
  - 2 end-members are sufficient to reproduce the experimental data of CJ2 glass, taking into account the precision of the data.
- **End-members Composition:**
  - Modeling results are “independent” of end-member composition when both are present.
- **Law of mass action:**
  - Can it describe disturbances and variations in elements concentrations?

Si + Al + Na ⇔ End-members

+Si   ΔS/V   +NaCl



SiAlNacj2 = 0.2231 H4(SiO4), 0.0284 Al[3+], 0.0284 Na[+], -0.1136 H[+], -0.3894 H_2O

- **Is the kinetic law of Graal functional?**
  - Can a single set of modeling parameters efficiently replicate all available data?

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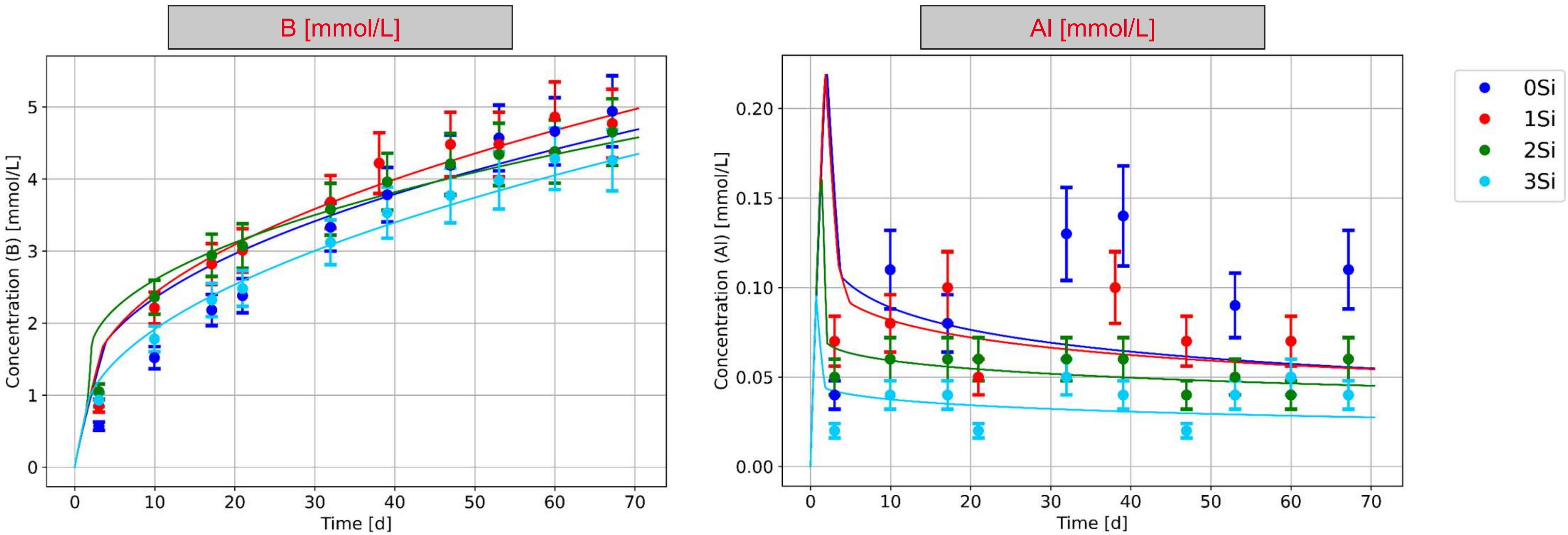
Variation in solution composition

- Initial addition of silicon (from 1 to 3 mmol/L , 90°C, S/V = 1cm^{-1}):



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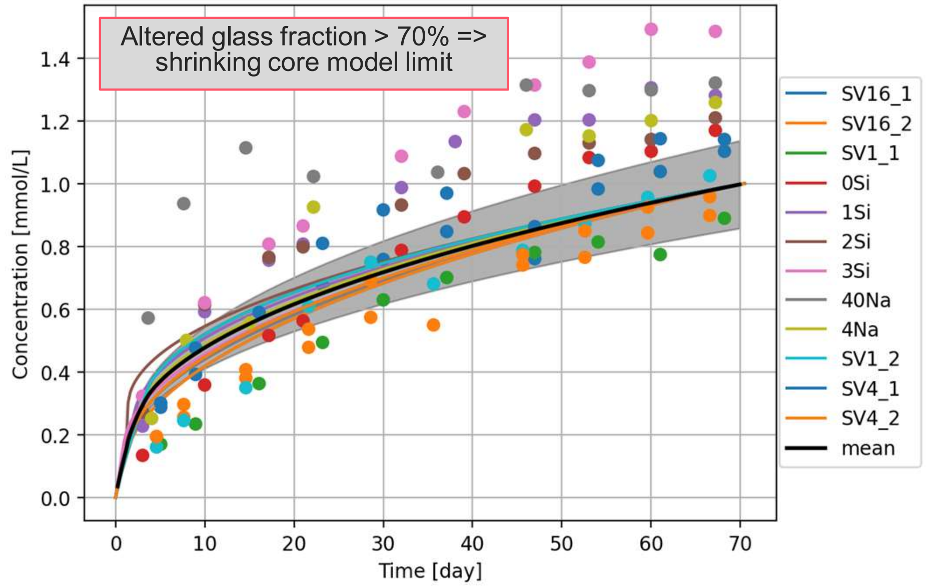
Modelling parameters

B [mmol/L]
Normalized concentrations



❖ **One set of parameters for modelling all experiments**

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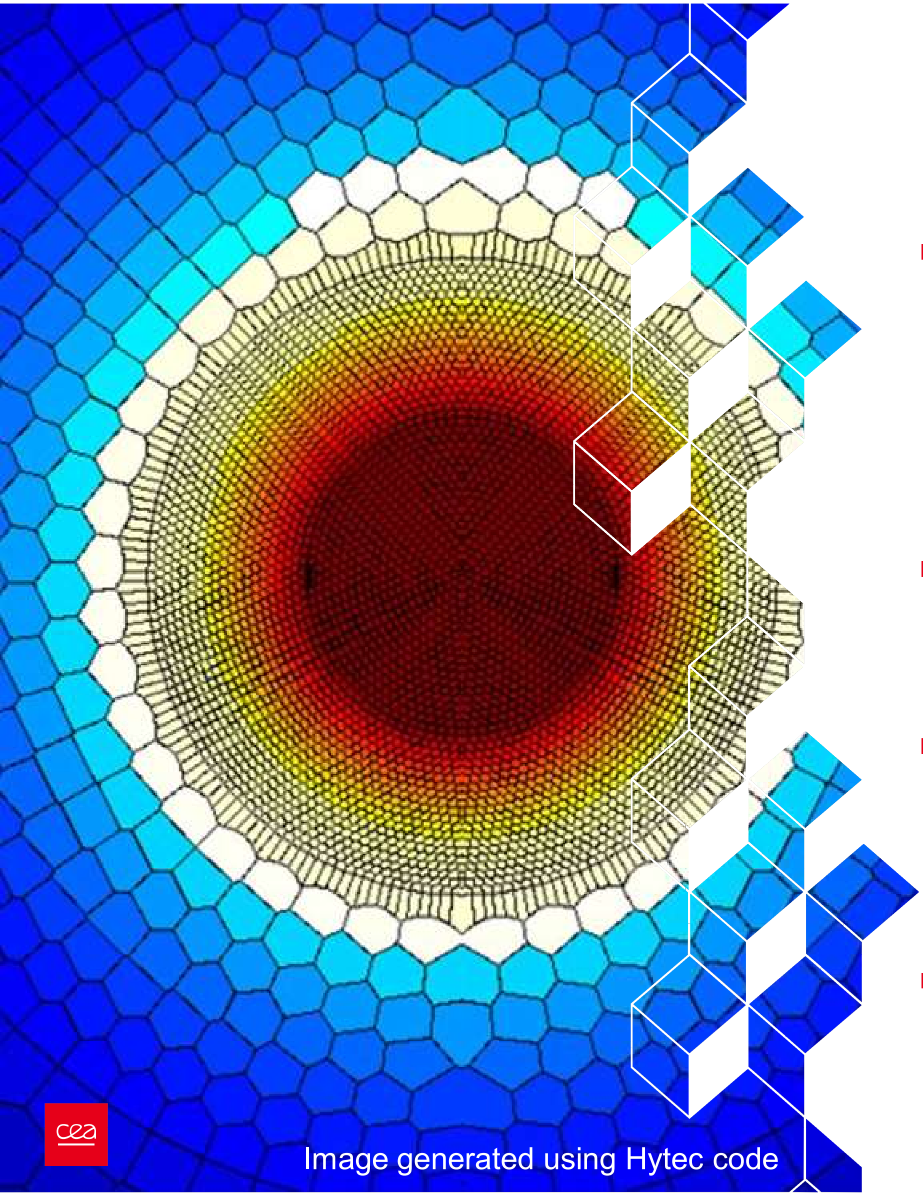


Why is GRAAL* useful ?

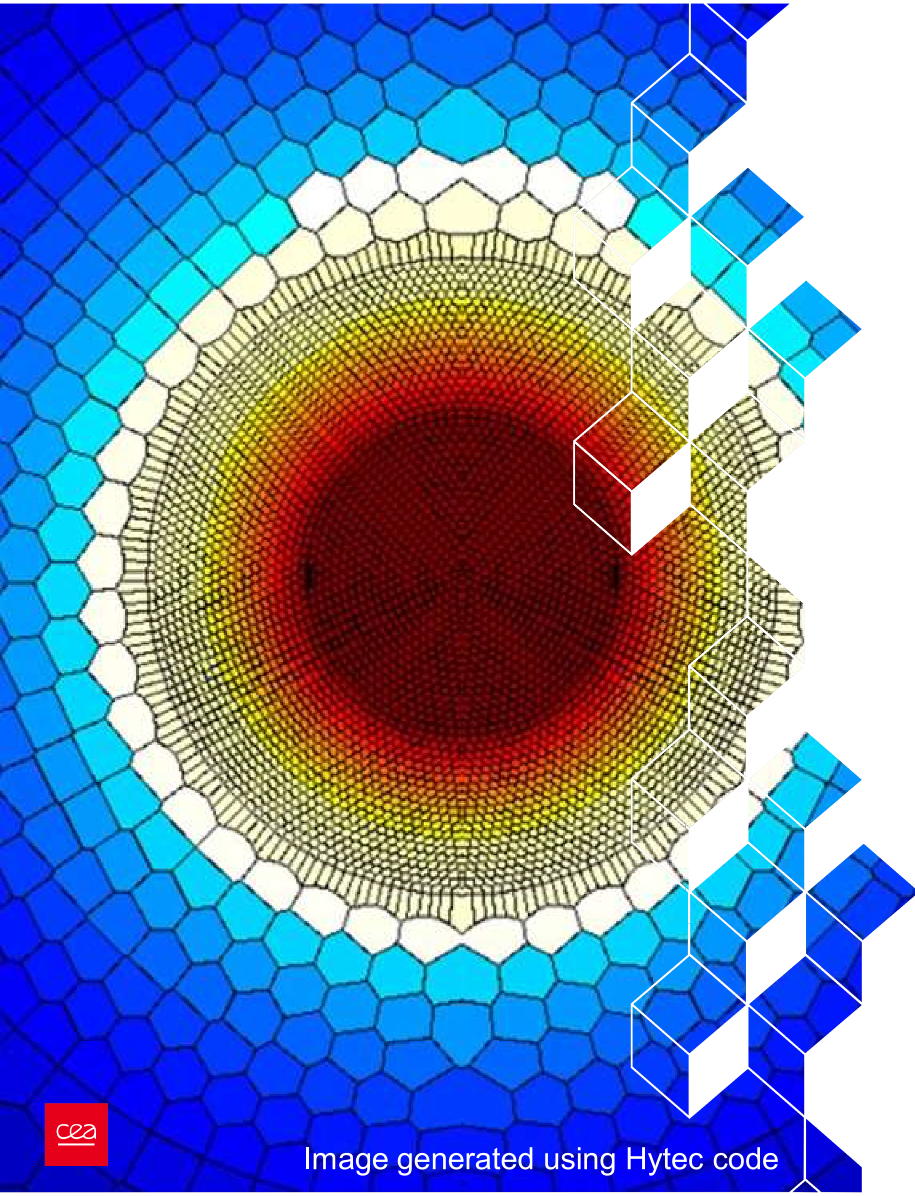
(* = as well as any model at RT codes scale)

- **Because it relies on**
  - Geochemical database
  - Efficient RT codes
  - A robust hypothesis : “the thicker the gel the slower the rate”
  - Accessible and therefore numerous experimental data (solution analysis & characterizations)

- **Because it can change scale**
  - And be applied both to lab and geological disposal time and space scales

- **Because it can be parameterized**
  - Limited number of parameters
  - Can be described across the entire domain of interest
    → Predictive modeling

- **Because it has proven useful**
  - In explaining experimental data especially integral experiments.



Thank you for your attention

Any question ? → pierre.frugier@cea.fr