



DE LA RECHERCHE À L'INDUSTRIE

Leila Galai

LABORATORY OF LONG TERM BEHAVIOR OF VITREOUS MATRICES

JOINT ICTP-IAEA INTERNATIONAL SCHOOL ON NUCLEAR WASTE VITRIFICATION



HIGH ACTIVITY STUDIES



GLASS FORMULATION



PROCESS DEVELOPMENT



LONG TERM BEHAVIOR

GEOLOGICAL REPOSITORY OF FRENCH HLW

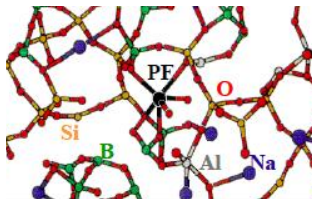
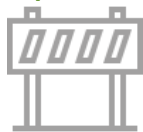
CIGÉO PROJECT : THE GEOLOGICAL STORAGE OF HLW DEVELOPED BY ANDRA



NATIONAL AGENCY FOR RADIOACTIVE WASTE MANAGEMENT



A MULTI-BARRIER CONCEPT :

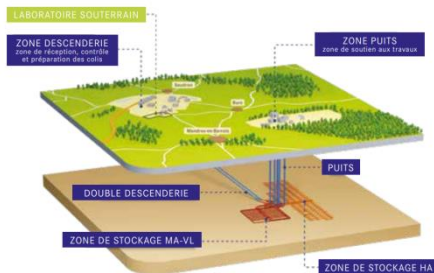


GLASS MATRIX POURED IN STAINLESS STEEL

CANISTER



LOW- ALLOYED STEEL OVERPACK



500-METER DEEP DISPOSAL

CALLOVO-OXFORDIAN (COX) CLAYSTONE

- Demonstrating the environmental safety of the concept : Assessing the long term behaviour of the nuclear glass

Understand the physical and chemical mechanisms that determine glass behavior under repository conditions

1

Description of repository condition key parameters

- ☐ Callovo-Oxfordian claystone fluid composition and its renewal
- ☐ Surrounding materials: clay, metal, cement

2

Quantification of the effect of these parameters on glass matrices life-time

- ☐ Parametric alteration experiments

3

Identification of **glass alteration mechanisms**

4

Modeling lab experiments

The inactive reference material is **SON68** glass.

This glass contains neither radioactive elements, which are instead simulated by other elements.

SON68 glass composition in oxide wt%

Oxide	wt%	Oxide	wt%	Oxide	wt%
SiO ₂	45.85	MoO ₃	1.78	CdO	0.03
Al ₂ O ₃	5.00	Cs ₂ O	1.12	SnO ₂	0.02
B ₂ O ₃	14.14	NiO	0.43	TeO ₂	0.23
Na ₂ O	10.22	P ₂ O ₅	0.29	BaO	0.62
CaO	4.07	SrO	0.35	La ₂ O ₃	0.93
Li ₂ O	1.99	Cr ₂ O ₃	0.53	Ce ₂ O ₃	0.97
ZnO	2.53	Y ₂ O ₃	0.20	Pr ₂ O ₃	0.46
ZrO ₂	2.75	MnO ₂	0.39	Nd ₂ O ₃	2.04
Fe ₂ O ₃	3.03	Ag ₂ O	0.03		

(Jollivet, 1995)

IDENTIFICATION OF GLASS ALTERATION MECHANISMS

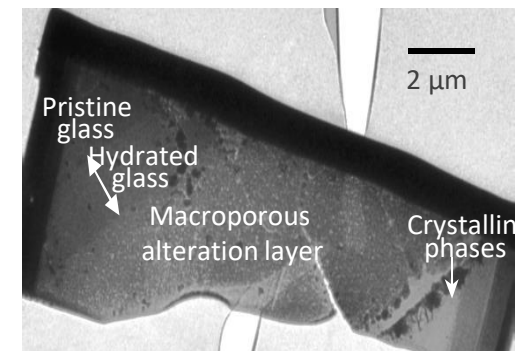
❖ Water: main cause of corrosion of the glass packages

- ❑ **Leaching experiments** in aqueous solutions, in contact with environmental materials
- ❑ Solution **analysis** and solid **characterization**

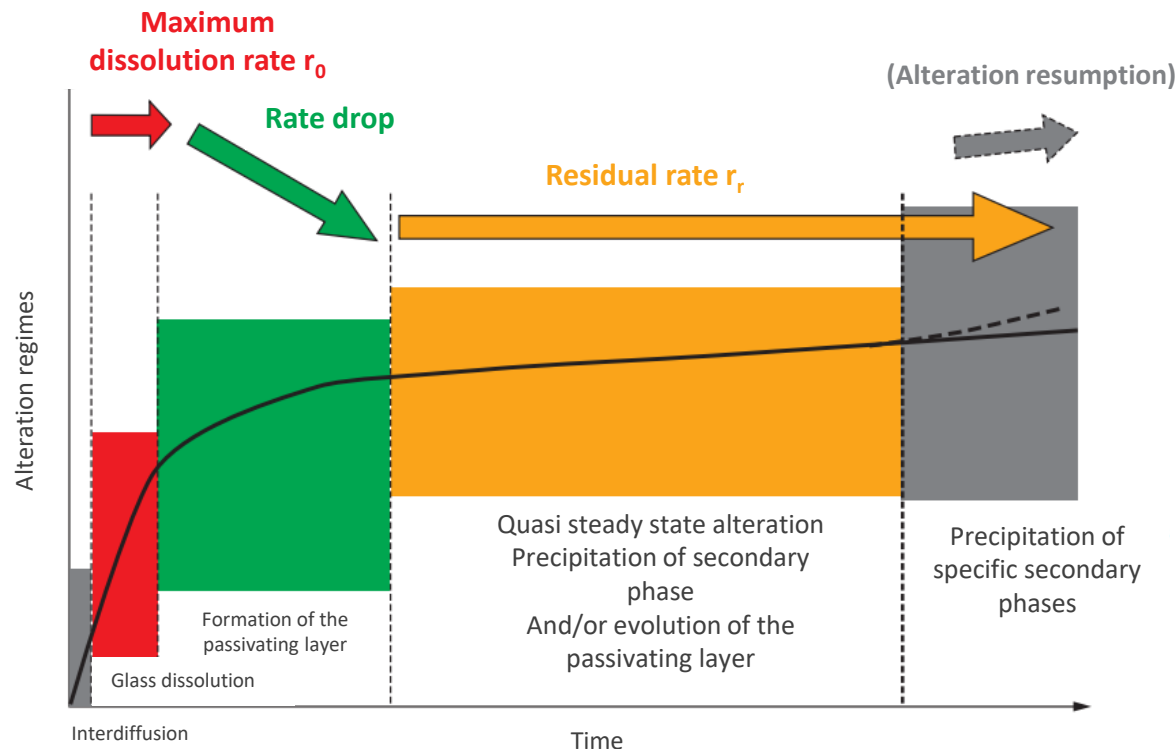
➤ Identify the nature and the properties of the alteration products

- HLW French reference glass rates

$$\begin{aligned}
 r_{0\ 100^{\circ}\text{C}} &\sim 1\ \mu\text{m/d} \\
 r_{0\ 50^{\circ}\text{C}} &\sim 10\ \text{nm/y} \\
 r_{r\ 90^{\circ}\text{C}} / r_{0\ 90^{\circ}\text{C}} &\sim 10\ 000
 \end{aligned}$$



Experimental evidence of a dense layer acting as a diffusion barrier and a hydrated glass that conserves glass structure



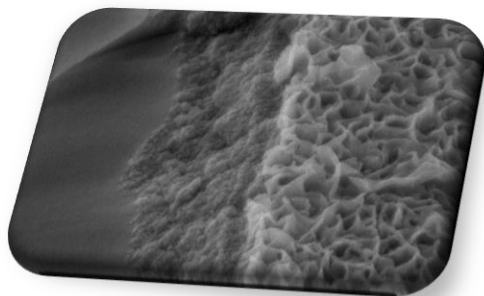
Geochemical Model

Macroscopic scientific models :
Justify assumptions of operational models

❖ GRAAL

Accounts for the diffusion and solubility in the gel, integrated with the reactive transport model HYTEC

- (Frugier et al. 2008)



Atomistic Models

Detailed mechanistic models :

- understand coupling at microscopic scale
- understand elementary mechanisms

❖ Monte Carlo ❖ Molecular dynamics ❖ Ab initio

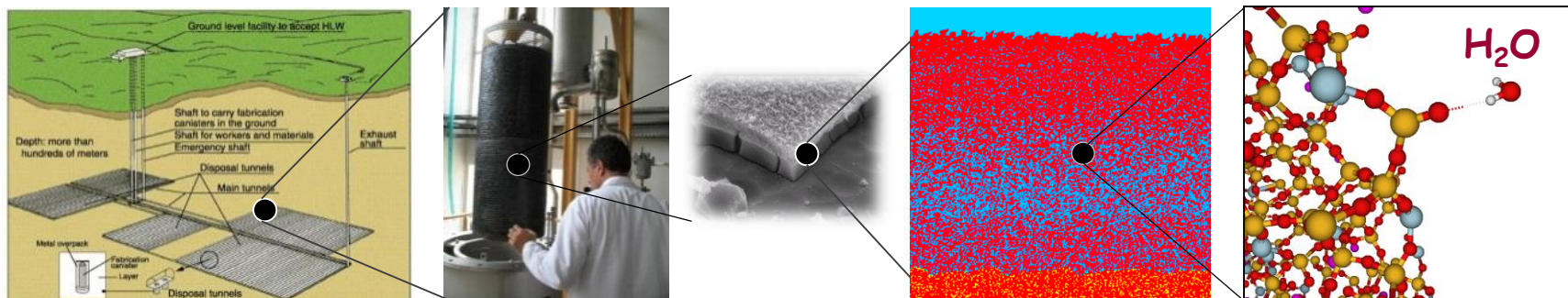
Model validations :

Natural and archaeological analogues of glasses attempt to answer the question of time scale



(Verney-Carron 2008)

To describe macroscopic properties...



... from atomic to mesoscopic scale



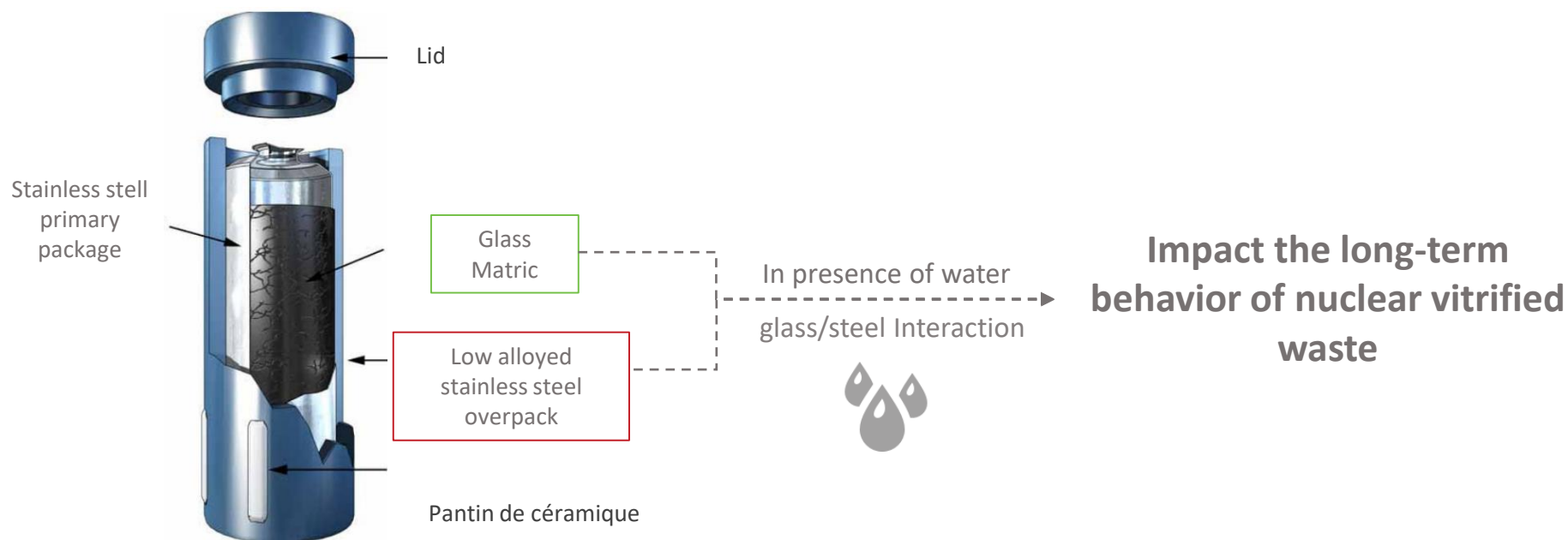
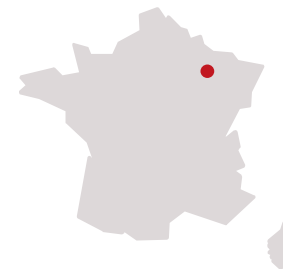
DE LA RECHERCHE À L'INDUSTRIE

STUDY OF REACTION MECHANISMS GOVERNING IRON- GLASS INTERACTION IN HLW DISPOSAL CONTEXT

Leila Galaï

➤ **LABORATORY OF LONG-TERM BEHAVIOR OF VITREOUS MATRICES**

CIGÉO PROJECT : THE GEOLOGICAL STORAGE OF HLW DEVELOPED BY ANDRA



Bring new insights into mechanisms governing the interaction between glass matrix and the stainless steel over-pack for a better prediction of the long term behavior of the nuclear glass under repository conditions

Glass-iron system: study of the effect of iron on glass alteration

*De Combarieu, 2007**Carrière, 2017**Burger et al., 2013**Frugier et al. 2007**Arena, 2016**Schegel et al., 2016**Mc Vay et al., 1983**Godon et al., 2013**Michelin et al., 2013**Brossel, 2017*

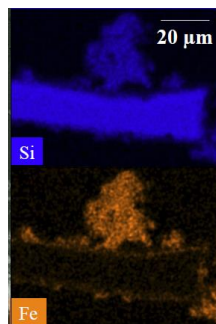
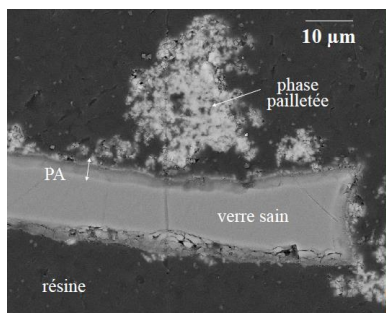
Increasing of glass
alteration in presence
of iron

+

Highlight the presence of
iron silicates

**Hypothesis**

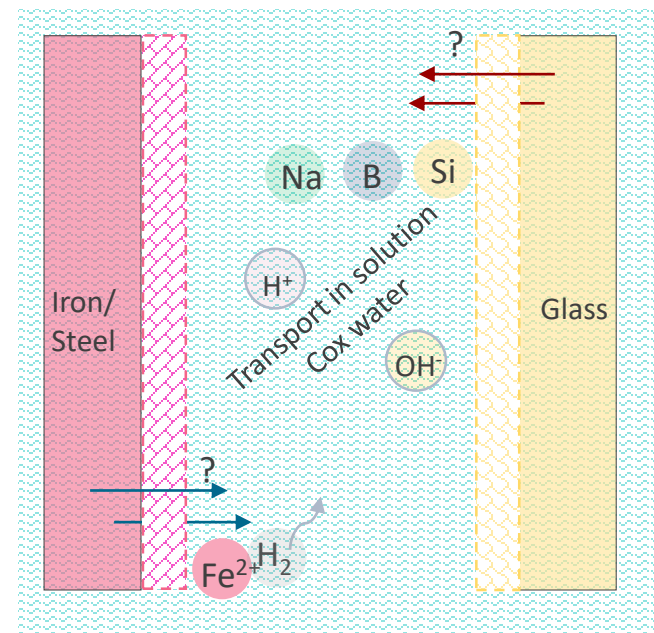
Si-Fe formation leads to a delay in
the saturation of the solution

**No adequate reference experience**

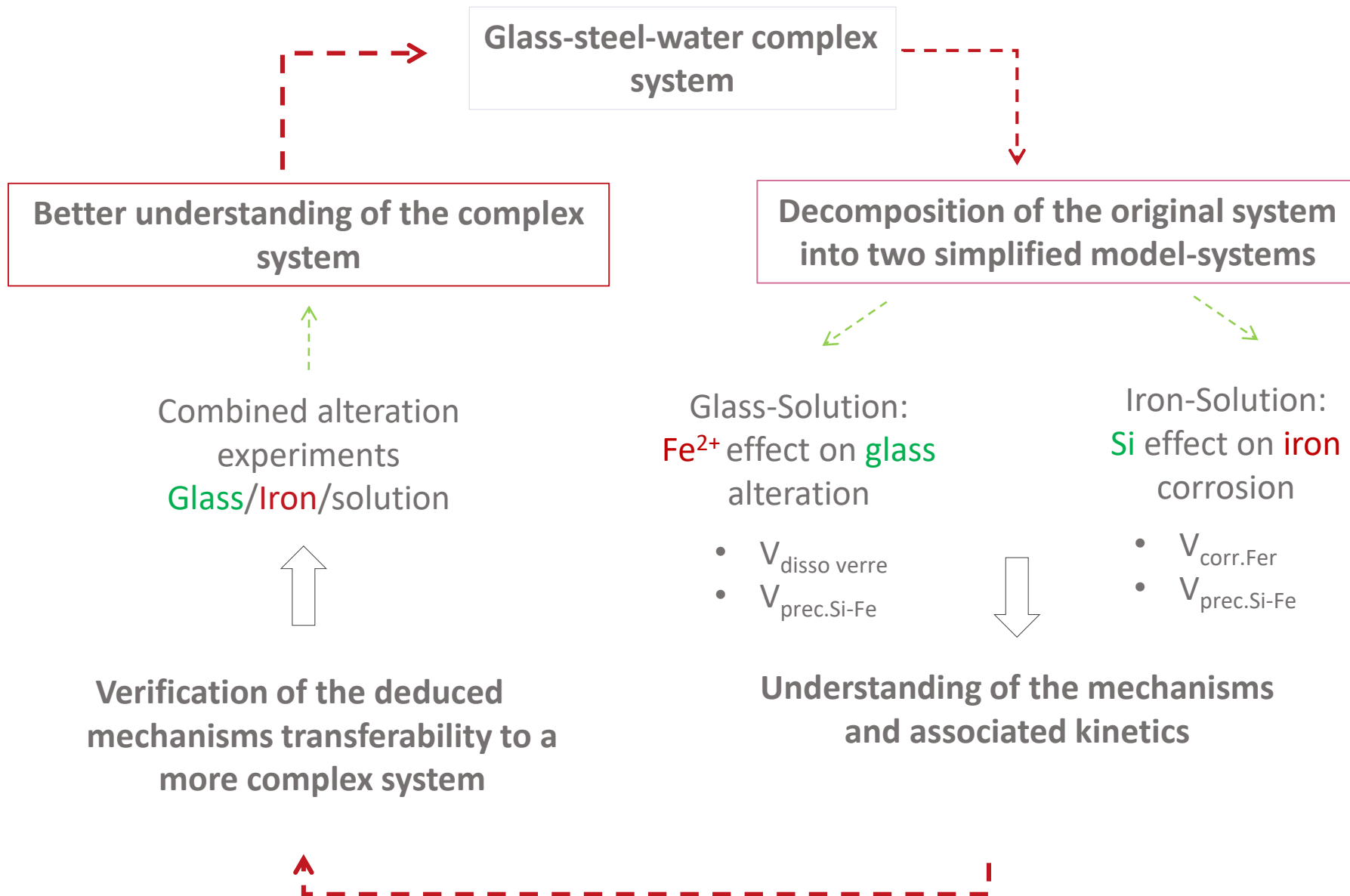
- No unambiguous conclusion on the effect of iron on the alteration of glass

**Simultaneous degradation of glass and iron / steel**

- Difficulty in identifying mechanisms on the surface of each material
- Poor literature on the effect of Si on Fe corrosion



Experimental systems too complex to allow a detailed understanding of the mechanisms governing the glass iron interaction

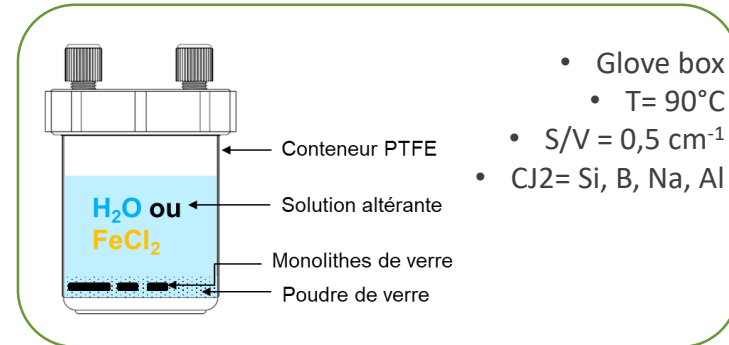


■ Study of Fe^{2+} effect on glass alteration kinetics

1. Free pH experiments

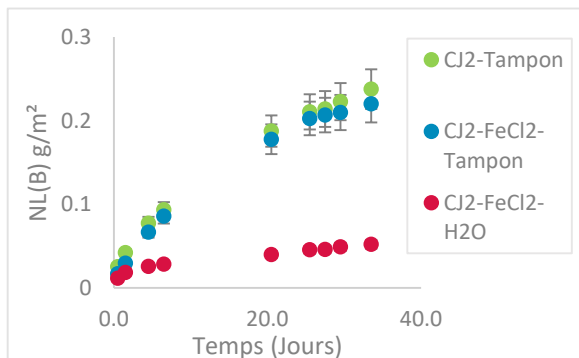
- Increasing of glass alteration in presence of FeCl_2

	H_2O	FeCl_2
pH	8,7	6,2
% Va	20	40



Need to work on the same pH to dissociate the effect of iron and pH on glass alteration

2. Buffered experiments: Buffer $\text{NH}_3/\text{NH}_4\text{Cl}$

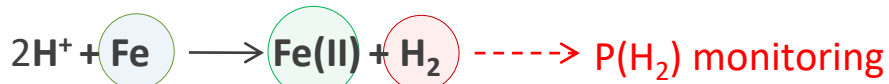


- Hides the possible effect of Fe^{2+} on glass alteration

Need to find an inert buffer towards glass alteration

- Study of Si effect on iron corrosion kinetics

- Iron Corrosion monitoring



- Sealed reactors to avoid gas leak



In solution

Si(IV)

H₂O/OH⁻...

• Iron oxide and hydroxide formation on the surface

➤ XPS Characterization

- Oxide layer thickness
- Fe²⁺ /Fe³⁺ ratio

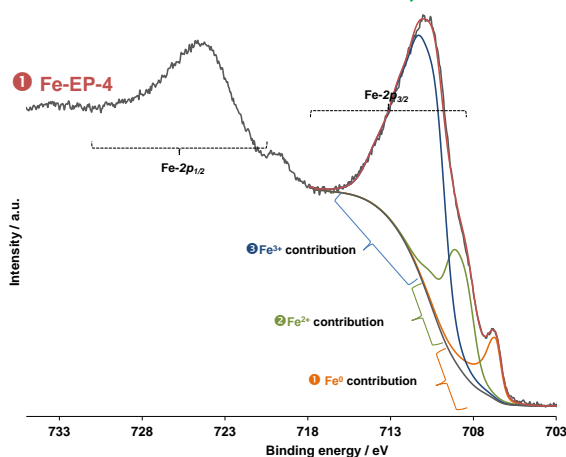
- Si-Fe formation
- Monitoring of Si consumption

- Iron oxide and hydroxide formation in solution

Fe²⁺ In solution

Iron corrosion experiments

- 4, 9 et 30 days
- pH 8
- T 50



Experience name	Duration (Days)	Oxide layer thickness (nm)
Fe- EP-4	4	5
Fe- EP-9	9	6
Fe- EP-30	30	6



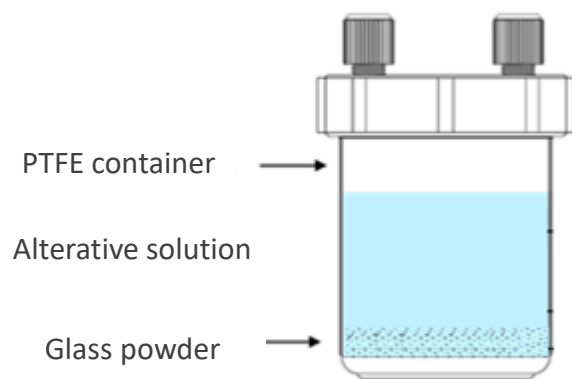
Oxide layer formed on the surface of Fe powder with little or no evolution in terms of composition and thickness

Study of iron corrosion kinetics possible only by solution analysis + characterization

Need to impose identical physicochemical conditions in all experiments

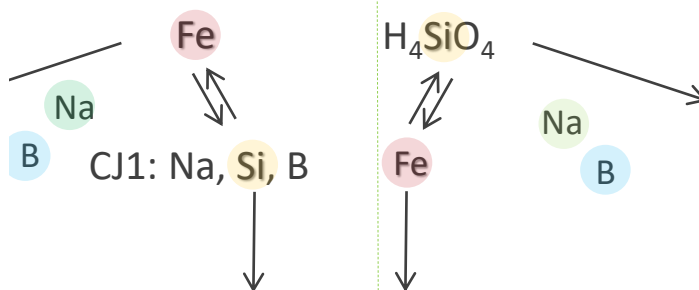
Glass solution system :

Fe effect on **glass**
alteration



- $V_{\text{disso verre}}$
- $V_{\text{prec.Si-Fe}}$

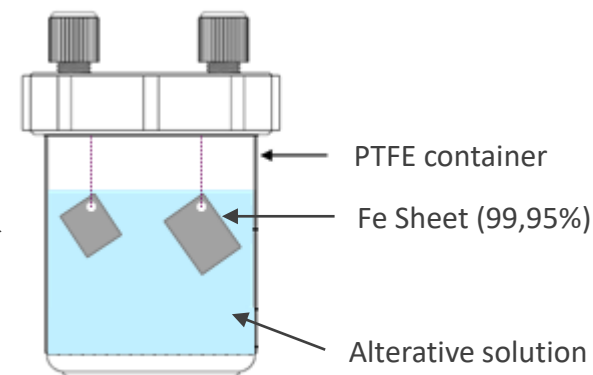
$T = 50\text{ }^{\circ}\text{C}$
 $\text{pH} = 8,2$
Borate buffer: H_3BO_3 , NaOH
Anoxic media (glove-box)



Identical physicochemical conditions:
Similar Si-Fe formed

Iron solution System :

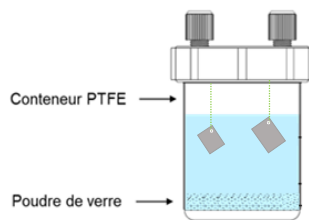
Si Effects on **iron**
corrosion



- $V_{\text{corr.Fer}}$
- $V_{\text{prec.Si-Fe}}$

Combined alteration experiments

Glass/Iron/solution



Modeling:

- Characterization: precipitated minerals nature and stoichiometry
- Kinetics of formation, Fe corrosion kinetics, glass alteration kinetics



Thank you for your attention

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- **Nicole Godon**